Nanoporous AuPt alloy with low Pt content: a remarkable electrocatalyst with enhanced activity towards formic acid electro-oxidation

Dongwei Li ^{a,b}, Fanhui Meng ^c, Hui Wang ^d, Xiaojian Jiang ^a, Ye Zhu ^{a,*}

^a School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China

^b State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

^c Tianjin Lishen Battery Joint-stock Co.,LTD, Tianjin 300384, China

^d Enviromental Protection Administration of Linyi, Linyi 276000, China

* Corresponding author:

Tel/Fax: +86-531-88363089.

Email address: zhuye@sdu.edu.cn (Y. Zhu)

Abstract

Highly active nanoporous AuPt (np-AuPt) alloys with Pt/Au molar ratio ranging from 0.5:99.5 to 5:95 were successfully synthesized based on dealloying strategy. The synthesized np-AuPt alloys consisted of three-dimensional bicontinuous ligament-pore structure (~10 nm) and microchannels. The electrochemical activity and stability of the np-AuPt alloys for formic acid electro-oxidation was investigated by tuning the Pt/Au molar ratio. Especially, a mass activity of the np-AuPt alloy that was 113 times higher than that of commercial JM-Pt/C catalyst was achieved at a Pt/Au molar ratio of 0.5:99.5. The low Pt/Au molar ratio made the surface Pt atoms be effectively isolated by the neighboring Au atoms, leading to the sole direct dehydrogenation pathway of the formic acid electro-oxidation on the np-AuPt alloys.

Keywords:

Formic acid electro-oxidation; AuPt alloy; Nanoporous; Ensemble effect

1. Introduction

Formic acid electro-oxidation (FAO) has attracted much attention in the past few decades, due to its potentially broad applications in the direct formic acid fuel cells (DFAFCs) and the relevant advantages including high theoretical open-circuit potential and low fuel crossover. To date, it has been proved that Pt-based catalysts can effectively catalyze FAO [1,2]. The general mechanism for FAO on Pt surface has been proposed as the so-called dual pathway: (1) the dehydrogenation of formic acid to CO_2 , with HCOO_{ads} as the reactive intermediate (direct oxidation pathway) and (2) the dehydration of formic acid to CO followed by subsequent oxidation of absorbed CO (CO_{ads}) to CO_2 (indirect oxidation pathway) [3,4]. Apparently, the dehydration pathway is undesirable, because the CO_{ads} intermediates easily poison the Pt surface and can only be oxidatively removed at high potentials. At present, many electrocatalysts (such as PtRu) could partly facilitate the oxidative removal of CO_{ads} generated in FAO, but could not completely resolve the problem of the CO poisoning [5]. What's more, most of the electrocatalysts would apparently suppress the direct oxidation pathway, slowing down the overall reaction. Therefore, innovation of Pt-based electrocatalysts with preference for the direct oxidation and elimination of the indirect oxidation would be of enormous significance for speeding up FAO. According to the theory of ensemble effect, which is defined as the arrangement of surface atoms of a particular pattern required for being active to a given kind of reactant molecules [6], one isolated Pt atom is active in the dehydrogenation pathway of formic acid, while the aggregation of three or more neighboring Pt atoms results in the

dehydration pathway with the formation of CO_{ads} [7]. Thus, it is believed that constructing Pt-based alloy with isolated Pt atoms could be an effective approach to promote the dehydrogenation pathway as well as suppress the dehydration pathway [8]. Among the series of alloys, AuPt alloy has attracted increasing interest, because gold surface favors the reductive deposition of Pt compared with other elements, and gold has the great chemical stability in formic acid. More importantly, it is recently pointed out that there is a significant shift of the d-band center from -2.25 eV for Pt to -1.80 eV for AuPt alloy, and the latter value is close to the d-band center of pure Pd (-1.83 eV), which is a well-known catalyst for FAO through the dehydrogenation pathway [9].

On the other hand, the morphology is a considerable factor affecting the activity of the catalyst. Up to now, AuPt alloy with different shapes has been developed, such as nanorods [10], nanowires [11], nanocables [12], and nanoporous films [13]. Among these various AuPt alloys, three-dimensional (3D) nanoporous materials with large specific surface area can provide a high density of active sites, leading to more efficient utilization of Pt. Furthermore, the interconnected channels extending in all three dimensions allow unblocked transport of heterogeneous molecules and electrons in the porous structure. Therefore, nanoporous AuPt (np-AuPt) alloys are worthwhile to be explored for effectively electrocatalyze FAO.

Several strategies have been pursued to prepare nanoporous materials, such as dealloying [14,15], surfactant-derived method [16-18], templating [6,19], and coating process [20]. Dealloying has been demonstrated to be very efficient in producing porous

alloys with bicontinuous ligament-pore structure. This process can effectively pre-define the bimetallic composition of the resulted nanoporous alloy with almost no loss of target metals. This is in sharp contrast to the other traditional approach of chemical synthesis where it is difficult to guarantee the composition of the resulted alloy as the same as the initial feed ratio in metal salts, mainly due to the different reduction rates of individual metal salts [21]. To our best knowledge, several groups have fabricated np-AuPt using dealloying method. For example, Snyder et al. prepared np-AuPt by dealloying of AuPtAg alloy, which exhibited ultrafine pore size and enhanced stability [14]. Xu et al. reported that selective leaching Cu from AuPtCu alloys in H_2SO_4 solution resulted in the formation of np-AuPt (np-Au₂₀Pt₈₀, np-Au₅₀Pt₅₀, and np-Au₈₀Pt₂₀), displaying surface sensitive reactivity towards FAO [15]. Zhang et al. fabricated np-Au₄₀Pt₆₀ alloys by dealloying of Au₁₀Pt₁₅Al₇₅ alloy in NaOH, HCl or NaCl solution, exhibiting superior catalytic activity towards FAO compared with commercial JM-Pt/C catalyst [22,23]. Although the specific activity of the previously reported np-AuPt was obviously enhanced, the mass activity was not outstanding due to high Pt content. For precious metal catalysts, the mass activity is as important as the specific activity, since the metals are priced by mass. And not only that, although the dehydrogenation reaction was significantly enhanced by most of the aforementioned np-AuPt catalysts, undesired dehydration reaction was still observed due to low dispersion of Pt atoms, which was directly resulted from the high Pt content. Accordingly, the fabrication of a novel

np-AuPt catalyst with low Pt content and high Pt dispersion is highly desired to improve the mass activity of the catalyst and suppress the dehydration pathway in FAO.

Since downsizing the Pt content in AuPt alloy may keep the Pt atoms highly dispersed [24], in this work, we focused on the preparation of np-AuPt catalysts with low Pt content by dealloying of AuPtAl precursors. For this purpose, the AuPtAl alloy precursors were deliberately designed by keeping the Pt/Au molar ratio no more than 5:95. The obtained np-AuPt alloys with varying Pt content were characterized by XRD, SEM and XPS. Their catalytic activity towards FAO was evaluated.

2. Experimental

2.1. Preparation of the np-AuPt alloys

The AuPtAl alloy precursors with varying AuPt compositions were prepared by melting elemental Al (purity, 99.99 wt. %), Pt (purity, 99.99 wt. %) and Au (purity, 99.99 wt. %) in a quartz crucible using a high-frequency induction furnace under an argon atmosphere. Using a single roller melt spinning apparatus, the pre-alloyed ingots were rapidly solidified into ribbons. The relative composition of Pt and Au was well controlled by adjusting the initial feed ratio. The dealloying of the AuPtAl alloy precursors was carried out in 4 M NaOH aqueous solution at room temperature (about 25 °C) for 24 h. The purple ternary alloys changed into golden binary alloys. The as-dealloyed samples were filtered out and thoroughly rinsed with distilled water until no NaOH was detected in the filtrate; and then dried in a vacuum desiccator at room temperature.

2.2. Preparation of the electrode

The catalyst suspension was prepared as follows: 3 mg fine ground as-dealloyed AuPt alloy, 200 μL isopropanol and 200 μL Nafion solution (0.5 wt. %) were mixed together and sonicated for 30 min to form a homogeneous suspension. Then, 10 μL of the catalyst suspension was drop coated onto a polished glassy carbon electrode (4 mm in diameter) and dried in the air for latter testing.

2.3. Characterization

Phase identification of the samples was conducted by X-ray powder diffraction (XRD) on a Bruker D8 advanced X-ray diffractometer with Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) at a scan rate of $0.02^\circ \text{ s}^{-1}$. The microstructure of the samples was characterized with scanning electron microscope (SEM, JEOL JSM-6700F), transmission electron microscope (TEM, JEOL JEM-2100F) and high-resolution TEM (HRTEM, JEOL JEM-2100F). Selected-area electron diffraction (SAED) was also used to document the crystalline nature of the samples. Element composition was analyzed by energy-dispersive spectrometer (EDS) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250). The content of Pt was accurately determined by an IRIS advantage inductively coupled plasma-atomic emission spectrometry (ICP-AES).

2.4. Electrochemical measurements

All electrochemical measurements were performed on a CHI 760D potentiostat in a

standard three-electrode cell at room temperature. A Pt plate ($1 \times 1 \text{ cm}^2$) and a mercury sulfate electrode (MSE) served as counter electrode and reference electrode, respectively. Prior to the measurements, the solutions were deaerated by bubbling with N_2 for at least 30 min. The working electrodes coated with as-dealloyed np-AuPt alloys or np-Au were first activated with cyclic voltammetry (CV) between -0.65 V and 1.1 V at 50 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ solution for 20 segments. Then, the electrocatalytic activity of the np-AuPt alloy-coated glassy carbon electrode towards FAO was evaluated in $0.5 \text{ M H}_2\text{SO}_4$ solution containing 0.5 M HCOOH by recording the linear sweep voltammogram (LSV) from -0.72 V to 0.6 V . The chronoamperometric curves were measured at -0.315 V for 2000 s.

2.5. CO stripping experiments

The CO stripping experiments were conducted according to the previous report [25]. CO was bubbled through $0.5 \text{ M H}_2\text{SO}_4$ electrolyte for 15 min at a fixed potential of -0.45 V to ensure sufficient CO adsorption onto the electrode surface. Subsequently, the electrolyte was deaerated with N_2 for 15 min to remove freely dissolved CO molecules. Finally, the CVs were recorded between -0.65 V and 0.65 V at 50 mV s^{-1} for two cycles. For comparison, commercial JM-Pt/C (60 wt. % Pt) catalyst was also measured under the identical experimental conditions.

3. Results and discussion

3.1. Characterizations of the AuPtAl alloy precursors

To obtain AuPt alloys with highly dispersed Pt atoms, four kinds of AuPtAl alloy precursors with the Pt content less than 5 at. % and one kind of AuAl alloy as control were prepared. For simplicity, the AuPtAl alloy precursors were denoted as $\text{Au}_{0.995}\text{Pt}_{0.005}\text{Al}_3$, $\text{Au}_{0.99}\text{Pt}_{0.01}\text{Al}_3$, $\text{Au}_{0.98}\text{Pt}_{0.02}\text{Al}_3$, and $\text{Au}_{0.95}\text{Pt}_{0.05}\text{Al}_3$, respectively in the light of the Au/Pt/Al atomic ratio. The bulk element composition was analyzed by EDS and summarized in Table s1 (see the Supporting Information). The Pt/Au ratios of the AuPtAl alloy precursors were determined to be around 05 : 99.5, 1 : 99, 2 : 98 and 5 : 95, respectively, and the overall Al content was at ~75 at. %, which was in good agreement with the original feed composition of the alloys. Fig. 1a shows the XRD patterns of the corresponding precursors in comparison with the reference profile of Al_2Au (PDF#17-0877). All the AuPtAl and AuAl precursors were composed of a single-phase intermetallic compound with an Al_2Au -type structure. Notably, the diffraction peak shifts towards high angles were observed for all AuPtAl precursors compared with those for AuAl precursor. Furthermore, these peak shifts increased with the increasing Pt content of the precursors. According to the previous reports [26], these peak shifts were resulted from the lattice contraction caused by the introduction of Pt. All the results demonstrated that Pt undoubtedly existed in the samples by replacing Au atom in the Al_2Au lattice and resulted in a single-phase alloy, though the content of Pt was quite low. According to the Debye-Scherrer equation (see the Supporting Information), the crystallite sizes of AuPtAl were calculated to be 37 ± 5 nm, comparable to that of the

AuAl precursor (about 42 nm), indicating that little percent of doping Pt atoms (≤ 5 at. %) had limited effect on the crystallite size.

3.2. Characterizations of the as-dealloyed AuPt alloys

The AuPt samples were prepared by selective leaching Al from the AuPtAl alloy precursors in NaOH solution. The Pt content in each as-dealloyed AuPt sample was determined by ICP-AES, based on which the total loading of Pt in each as-dealloyed AuPt sample was calculated to be almost the same as the feeding content of Pt in the initial precursors. It was shown that Pt was almost not lost during the dealloying process. Besides, the bulk composition of the as-dealloyed AuPt samples was analyzed by EDS ([Table s1, see the Supporting Information](#)), which exhibited the similar Au/Pt atomic ratio with that in the initial precursors. [According to the dealloying mechanism \[27\], the residual Al \(several atom percent\) was detectable in the as-dealloyed sample. Since the presence of Al has no effect on the FAO,](#) the samples were designated as Au_{99.5}Pt_{0.5}, Au₉₉Pt₁, Au₉₈Pt₂, and Au₉₅Pt₅ for simplicity in the light of the Au/Pt atomic ratio.

XPS were conducted to characterize the electronic structures of the AuPt samples, as shown in Fig. 2. The binding energy of the Au-4f_{7/2} peak for Au_{99.5}Pt_{0.5}, Au₉₉Pt₁, Au₉₈Pt₂ and Au₉₅Pt₅ was at 84.02, 84.05, 84.15 and 84.16 eV, respectively, revealing gradual shift to high binding energy with the increasing Pt content, as compared with 84.0 eV for Au dealloyed from AuAl alloy precursor (Fig. 2a). For

all the AuPt samples, the spectrum of Pt-4f peak was deconvoluted into three components, including Pt(0), Pt(II) as well as Pt(IV) oxidation states (the detailed discussion was in the Supporting Information, Table s2). Meanwhile, the 4f_{7/2} peak of Pt(0) for Au_{99.5}Pt_{0.5}, Au₉₉Pt₁, Au₉₈Pt₂ and Au₉₅Pt₅ was at 70.95, 71.00, 71.04 and 71.13 eV, respectively, which exhibited a slight upshift with the increasing Pt content. These binding energy shifts suggested that Au and Pt in the samples were atomically mixed with no phase separation at the surface of the AuPt samples, and the shift could be ascribed to the electron effect and the geometric effect by the alloying [6]. Similar binding energy shifts were observed for AuPt alloy foam fabricated by the hydrogen bubble dynamic template [6] and co-reduction under microwave condition [28]. However, different variation trend was reported for AuPt alloy as the Pt content was high [15]. This phenomenon is acceptable, because binding energy shift may be affected by composition, phase segregation and strain effect [29,30]. The surface composition of the AuPt alloys was semiquantitatively calculated with the peak area and the sensitivity factor of Au, Pt and Al based on XPS spectra (Table s1, see the Supporting Information). Comparing the surface composition with the bulk composition, a certain degree of Al enrichment in the near surface region was observed. The preferential segregation of Al to the surface is understandable because the formation of more stable oxide provides the driving force for such kind of surface segregation, which is frequently observed in other alloy nanostructures [31].

XPS is a surface sensitive technique, which probes only thin layers of nanometers. In order to further determine the feature of bulk phase, the AuPt samples were characterized by XRD. Fig. 1b shows the XRD patterns of the prepared AuPt samples ($\text{Au}_{99.5}\text{Pt}_{0.5}$, $\text{Au}_{99}\text{Pt}_1$, $\text{Au}_{98}\text{Pt}_2$ and $\text{Au}_{95}\text{Pt}_5$) in comparison with the Au sample dealloyed from AuAl alloy precursor. Obviously, only one set of broad diffraction peaks was observed, which could be assigned to the (111), (200) and (220) reflections from a face-centered cubic (fcc) structure. The XRD patterns in the range between 37.6° and 40.6° in Fig. 1b are enlarged as the insets. Careful comparison revealed that the peaks of $\text{Au}_{99.5}\text{Pt}_{0.5}$, $\text{Au}_{99}\text{Pt}_1$, $\text{Au}_{98}\text{Pt}_2$ and $\text{Au}_{95}\text{Pt}_5$ samples were located between the (111) peaks of Au (PDF#04-0784) and Pt (PDF#04-0802), additionally, the peak positions gradually shifted to the pure Pt side with the increasing Pt content, suggesting that the as-dealloyed AuPt samples are, indeed, a single-phase alloy material rather than a mixture of monometallic Au and Pt or a core-shell structure of Au and Pt [32]. It has been well known that bimetallic AuPt nanoparticles are inclined to form core-shell structure with segregated Au on the surface, especially when the Pt content is low [33]. Interestingly, during dealloying process, the surface diffusion and reorganization of Au/Pt contribute to the formation of the AuPt alloy even containing low content of Pt, which is favorable for heterogeneous electrocatalysis of FAO [34].

To study the morphology of the as-dealloyed AuPt samples, they were grinded and then examined with electron microscope. Fig. 3a1 and a2 show the plan-view microstructure of the $\text{Au}_{99.5}\text{Pt}_{0.5}$ alloy. Obviously, the porous structure resembled that of the np-Au which was produced by dealloying of the AuAl alloy under the same dealloying condition (Fig. s2, see the Supporting Information). At low magnification (Fig. 3a1), islands in the size of several microns were observed, forming interisland microchannels. A closer inspection on an individual island was conducted at a higher magnification (Fig. 3a2), which exhibited an open, bicontinuous interpenetrating ligament-pore structure with a ligament size around 10 nm, smaller than that of the np-Au (around 15 nm, Fig. s2b, see the Supporting Information). The change in ligament size was due to the low diffusivity of Pt, which would have a “pinning effect” on the diffusivity of Au [14]. These open nanopores are readily accessible to the reactant molecules in electrocatalytic reaction. In addition, a typical TEM image provided more details about the structure, where the clear contrast between dark skeletons (ligaments) and inner bright regions (pores) further confirmed the formation of a bicontinuous nanoporous structure (Fig. 3a3). The selected-area electron diffraction (SAED) image revealed a single crystal pattern of the np- $\text{Au}_{99.5}\text{Pt}_{0.5}$ recorded along the [110] zone axis direction across the whole selected area (inset of Fig. 3a3). Fig. 3a4 shows a typical HRTEM image of this structure, where the lattice fringes were observed extending throughout all the ligaments and the lattice spacing was

calculated to be 0.234 nm. This value was in good agreement with the d value of the (111) crystalline planes of the fcc Au (0.235 nm). The slight difference in the lattice parameter was ascribed to the co-existence of Pt atoms, as strongly supported by the XRD characterization. The crystallite size of np-Au_{99.5}Pt_{0.5} sample, roughly calculated from the Debye-Scherrer equation, was about 12 nm, which agreed well with that obtained from TEM image. As shown in Fig. 3b1–d4, the as-dealloyed np-Au₉₉Pt₁, np-Au₉₈Pt₂ and np-Au₉₅Pt₅ also exhibited similar 3D bicontinuous porous structures with microchannels. The ligament sizes were 10±3 nm, comparable to that of the np-Au_{99.5}Pt_{0.5}. Perhaps the little percent of doping Pt atoms (≤ 5 at. %) had limited effect on the modulation of the ligament scale in the as-dealloyed np-AuPt alloys, which was in good agreement with the value reported by Erlebacher et al [14]. STEM-EDX elemental mapping was used to investigate the Pt distribution in np-AuPt sample. np-Au₉₅Pt₅ was chosen as the representation. Fig. s3 in the Supporting Information shows the STEM image of np-Au₉₅Pt₅ and the corresponding elemental maps for Au and Pt. Au was distributed throughout the ligament, the density of Pt was obviously lower than that of Au. Although the Pt loading was quite low, the overlap region of Au and Pt for this sample exhibited high distribution of Pt on the sample ligament (Fig. s3d in the Supporting Information). Considering the ultralow ratio of Pt/Au, we inferred that the dispersion of Pt in the np-AuPt alloys might be at the atomic level. As demonstrated above, the AuPt alloys with low Pt content and nanoporous structure have been prepared successfully. It is therefore of practical

importance to investigate whether the np-AuPt alloys with low Pt content possess exceptional electrocatalytic activity for FAO as we conceived.

3.3 Electrochemical characterization of the np-AuPt alloys

CV is a surface sensitive technique used to assess the electrochemical properties of surface atoms. After the activation with CVs for 20 segments, CVs for the activated np-AuPt alloys and np-Au were recorded in 0.5 M H₂SO₄ solution, as shown in Fig. 4. The CVs for the np-AuPt alloys revealed hydrogen adsorption/desorption (under-potentially deposited hydrogen, H_{upd}) in the potential region between -0.65 V and -0.44 V (vs. MSE), indicating the presence of Pt component in the as-dealloyed samples [8]. In the reverse scan, the CV for the np-Au only showed a single reduction peak at about 0.46 V, which was related to the reduction of Au oxides; whereas two well-separated peaks were observed for the np-AuPt alloys: the large one around 0.43 V was ascribed to the reduction of Au oxides, and the other small one around 0–0.05 V was attributed to the reduction of Pt oxides, which were consistent with the previously reported literatures [35]. Moreover, the reduction peak current for Pt oxides gradually increased with the increasing Pt content, further indicating that Pt has been efficiently doped into the samples. Besides, the reduction peak of Pt oxide shifted to a lower potential with the increase of Pt content, which was caused by the interaction between Pt and Au [6,36]. The similar electronic modification effect of Au on Pt also has been

reflected from the XPS.

3.4 Electrocatalytic activity of the np-AuPt alloys for FAO

After the activation in H_2SO_4 , the electrocatalytic activity of the np-AuPt alloys and commercial JM-Pt/C for FAO was evaluated by CVs and LSVs. The mass current density was normalized to the actual Pt loading on each electrode that was accurately deduced by the results of ICP-AES (Table 1). As shown in Fig. 5a, the CV of FAO obtained on commercial JM-Pt/C shows a large difference between the forward and reverse scan. In the forward scan, the first peak around -0.1 V was ascribed to the direct oxidation of formic acid via the dehydrogenation process, while the second peak at 0.26 V was related to the oxidation of CO_{ads} species that were generated from the dehydration process [37]. The ratio of the peak current densities between the second and the first peak was 4.1, revealing that the dehydration mechanism dominated this electrocatalysis. During the reverse scan, all the poisoning species (CO_{ads}) were oxidized at high potential and FAO then can occur on the clean Pt surface [38]. The large difference between the forward and reverse scan suggested the severe poisoning of catalytic sites by CO_{ads} . Instead of the reverse scan, we focus our observation on the evolution of anodic current during the forward scan, as the FAO process in the forward scan was closer to the real situation [39]. For all the np-AuPt alloys, the observed high current density at about -0.15 V and complete suppression of the second peak at 0.26 V was associated with the direct oxidation path (Fig. 5b). Taking the present Pt/Au atomic ratio into consideration,

it can be inferred that the surface Pt atoms has been effectively isolated by the neighboring Au atoms on the Au-rich surface layer, thereby leading to the sole direct dehydrogenation pathway of FAO. Meanwhile, slight difference in the current density was observed between the forward and reverse scan, indicating that np-AuPt alloys did not cause any drastic change during the FAO process at the upper potential limit, essentially because poisonous CO_{ads} formation was not involved in the FAO [40].

For simplicity and better comparisons, the electrocatalytic activity was evaluated by the first scans of LSVs from -0.72 V to 0.6 V (Fig. 5c). The mass current density for Au_{99.5}Pt_{0.5}, Au₉₉Pt₁, Au₉₈Pt₂, Au₉₅Pt₅ and the commercial JM-Pt/C was 7.01, 5.92, 4.51, 4.95 and 0.062 A mg_{Pt}⁻¹, respectively. The mass activity of the np-Au_{99.5}Pt_{0.5} sample was almost 113 times higher than that of the commercial JM-Pt/C, which was comparable with the previous works [41,42]. The outstanding mass activity can be explained with the following reasons. Np-Au_{99.5}Pt_{0.5} has ultralow Pt loading (0.25 μg Pt/electrode), which directly resulted in the high-usage of Pt and high mass current density. On the other hand, recent theoretical and experimental results demonstrated that the isolated Pt atoms can exhibit outstanding catalytic activity, much higher than close-packed Pt atoms [43, 44]. The low Pt/Au molar ratio made the surface Pt atoms be effectively isolated by the neighboring Au atoms, leading to remarkable electrocatalytic activity for FAO with high apparent current.

To evaluate the specific activity of the np-AuPt alloys towards FAO, the specific current density was normalized to the electrochemically active surface areas (ECSAs) of Pt [45]. Table 1 shows the ECSAs of Pt, which were calculated from the CVs in Fig. 4 by measuring the hydrogen absorption/desorption charge at Pt with converting the electric charge density for hydrogen adsorption ($210 \mu\text{C cm}^{-2}$) [46]. Compared with the commercial JM-Pt/C, the np-AuPt alloys have smaller ECSAs, because some Pt atoms were buried below the surface [22]. The peak current densities for the $\text{Au}_{99.5}\text{Pt}_{0.5}$, $\text{Au}_{99}\text{Pt}_1$, $\text{Au}_{98}\text{Pt}_2$, $\text{Au}_{95}\text{Pt}_5$ and commercial JM-Pt/C were 10.22, 7.82, 6.09, 2.57 and 0.82 mA cm^{-2} , respectively (Fig. 5d). Table 2 lists the electrocatalytic performance of different AuPt nanocatalysts and the commercial JM-Pt/C for FAO. It was noted that all the np-AuPt alloys prepared in this work exhibited superior electrocatalytic activity in terms of both mass activity and specific activity. The improved electrocatalytic activities of the np-AuPt alloys are highly valuable, because lots of well-defined Pt-containing nanostructures exhibited an enhanced specific activity, however, a decrease in Pt mass activity (such as Pt concave nanocubes [50] and multioctahedrons [51]). For the previously reported np-AuPt alloys with high Pt content [22,23], although the dehydrogenation reaction was significantly enhanced, undesired dehydration reaction was still observed. Obviously, the np-AuPt alloys prepared in this work were superior to the most of the previously reported np-AuPt alloys.

These results unambiguously demonstrate that our samples have excellent electrocatalytic performance towards FAO. This improved electrocatalytic activity can be explained with the ensemble effect, where isolated Pt atoms are crucial for the direct pathway of FAO. As expected, the obtained np-AuPt alloys undoubtedly meet the needs for the direct dehydrogenation path. Furthermore, it is worthwhile to mention that, among the obtained np-AuPt alloys, the np-Au_{99.5}Pt_{0.5} alloy had the lowest Pt content and the smallest ECSA, however, exhibited the outstanding catalytic activity. Similar phenomenon has been observed for Pt-modified nanoporous gold and Pt deposited Au (111) [52].

3.5 Electrochemical CO stripping test of the np-AuPt alloys

To further prove the inhibition of the poisonous CO formation on the as-dealloyed np-AuPt alloys, CO stripping test was conducted. The corresponding voltammograms of the prepared catalysts are presented in Fig. 6a-e, where the currents in the voltammograms were normalized to the electrode geometric area, as reported in ref. [25]. Since all the CO_{ads} on the surface of electrodes had been oxidized in the first positive potential sweep (the solid curve) and there was no freely dissolved CO remained in the bulk electrolyte due to the absolutely purging by N₂, the subsequent sweep (the dotted curve) was only related to the intrinsic electrochemical performance of electrodes surface. Therefore, the difference of the first positive scan from the second positive scan completely reflected the oxidation

of CO_{ads} . For the commercial JM-Pt/C, the oxidation peak of CO_{ads} was observed at about 0.2 V through careful comparison (Fig. 6a), which was consistent with the previous reports [23]. Obviously, the oxidation peak in the similar potential range appeared for the JM-Pt/C in Fig.5, indicating that poisonous CO_{ads} formed in the FAO on the JM-Pt/C, which has been demonstrated in the previous reports [53]. In contrast, the peak of CO_{ads} electro-oxidation on np-AuPt alloys appeared at about 0.45 V (Fig. 6b-e). This positive shift was associated with a special surface state of Pt, where highly dispersed Pt atoms did not possess enough neighboring Pt atoms and the alloying effect increased the bonding energy between Pt and CO [54]. Notably particularly, for np-AuPt alloys, the CO_{ads} oxidation peak around 0.45 V didn't appear in the corresponding potential range in the FAO (Fig. 5), indicating that poisonous CO_{ads} formation was not involved in the FAO on np-AuPt alloys, further demonstrating that the remarkable catalytic performance of np-AuPt alloys for FAO was attributed to the preference for the direct oxidation and elimination of the indirect oxidation.

3.6 Steady-state activity towards FAO

The stability is very important to the catalyst, therefore, we investigated the catalytic stability of the np-AuPt alloys towards FAO by chronoamperometric measurement under a constant potential of -0.315 V for 2000 s (Fig. 7). It was observed that, after 2000 s, the oxidation current densities (final activity) for

Au_{99.5}Pt_{0.5}, Au₉₉Pt₁, Au₉₈Pt₂, Au₉₅Pt₅ and commercial JM-Pt/C were 2.67, 1.40, 0.67, 0.17 and 0.075 mA cm⁻², corresponding to 48%, 43%, 34%, 15%, and 22% of their initial maximum values, respectively. This final activity of the np-Au_{99.5}Pt_{0.5} was about 36 times as high as that of the commercial JM-Pt/C. This great stability could be attributed to the ensemble effect on the AuPt surface with no CO formation during FAO [53]. The above results indicated that the electrocatalytic activity and stability of the np-Au_{99.5}Pt_{0.5} were the best among the catalysts prepared in this paper.

4. Conclusions

In summary, the np-AuPt alloys with low Pt content (≤ 5 at. %) were firstly prepared by one-step dealloying method. The synthesized np-AuPt alloys consisted of 3D bicontinuous ligament-pore structure (~10 nm) and microchannels, which displayed superior electrocatalytic activity and long stability for FAO. The superior activity was attributed to the preference for the direct oxidation and elimination of the indirect oxidation, which was demonstrated by the results of FAO and CO stripping test. Compared with the commercial JM-Pt/C, np-Au_{99.5}Pt_{0.5} alloy exhibited significantly improved specific activity, mass activity and enhanced stability for FAO, suggesting great potential for the application in the DFAFCs.

Acknowledgments

This work was sponsored by the National Science Foundation of China (51171092, 21305077), the Research Fund for the Doctoral Program of Higher Education of China (20090131110019), the Research Award Fund for Outstanding Middle-aged and Young Scientist of Shandong Province (BS2013SW031), the China Postdoctoral Science Foundation (2013M531585), and the Independent Innovation Foundation of Shandong University (2012HW004).

References

- [1] N. Tian, Z.Y. Zhou, S.G. Sun, Y. Ding, Z.L. Wang, Synthesis of tetrahedral platinum nanocrystals with high-index facets and high electro-oxidation activity, *Science* 316 (2007) 732-735.
- [2] H. Lee, S.E. Habas, G.A. Somorjai, P.D. Yang, Localized Pd overgrowth on cubic Pt nanocrystals for enhanced electrocatalytic oxidation of formic acid, *J. Am. Chem. Soc.* 130 (2008) 5406-5407.
- [3] X.W. Yu, P.G. Pickup, Recent advances in direct formic acid fuel cells (DFAFC), *J. Power Sources* 182 (2008) 124-132.
- [4] M. Osawa, K-i Komatsu, G. Samjeské, T. Uchida, T. Ikeshoji, A. Cuesta, C. Gutiérrez, The role of bridge-bonded adsorbed formate in the electrocatalytic oxidation of formic acid on platinum, *Angew. Chem. Int. Ed.* 50 (2011) 1159-1163.
- [5] C. Rice, S. Ha, R.I. Masel, A. Wieckowski, Catalysts for direct formic acid fuel cells, *J. Power Sources* 115 (2003) 229-235.

- [6] J. Liu, L. Cao, W. Huang, Z.L. Li, Preparation of AuPt alloy foam films and their superior electrocatalytic activity for the oxidation of formic acid, *ACS Appl. Mater. Interfaces* 3 (2011) 3552-3558.
- [7] A. Capon, R. Parsons, The oxidation of formic acid at noble metal electrodes: I. Review of previous work, *J. Electroanal. Chem.* 44 (1973) 1-7.
- [8] M. Gong, F. Li, Z. Yao, S.Q. Zhang, J.W. Dong, Y. Chen, Y.W. Tang, Highly active and durable platinum-lead bimetallic alloy nanoflowers for formic acid electrooxidation, *Nanoscale* 7 (2015) 4894-4899.
- [9] W.P. Zhou, A. Lewera, R. Larsen, R.I. Masel, P.S. Bagus, A. Wieckowski, Size effects in electronic and catalytic properties of unsupported palladium nanoparticles in electrooxidation of formic acid, *J. Phys.Chem. B* 110 (2006) 13393-13398.
- [10] Z.K. Zheng, T. Tachikawa, T. Majima, Plasmon-enhanced formic acid dehydrogenation using anisotropic Pd-Au nanorods studied at the single-particle level, *J. Am. Chem. Soc.* 137 (2015) 948-957.
- [11] W. Lu, J. Ge, L. Tao, X. Cao, J. Dong, W. Qian, Large-scale synthesis of ultrathin Au-Pt nanowires assembled on thionine/graphene with high conductivity and sensitivity for electrochemical immunosensor, *Electrochimica Acta* 130 (2014) 335-343.
- [12] J. Yoon, H. Baik, S. Lee, S.J. Kwon, K. Lee, One-pot synthesis of ultralong coaxial Au@Pt nanocables with numerous highly catalytically active perpendicular twinning boundaries and Au@Pt core-shell bead structures, *Nanoscale* 6 (2014) 6434-6439.

- [13] H.J. Jin, X.L. Wang, S. Parida, K. Wang, M. Seo, J. Weissmüller, Nanoporous Au-Pt alloys as large strain electrochemical actuators, *Nano Lett.* 10 (2010) 187-194.
- [14] J. Snyder, P. Asanithi, A.B. Dalton, J. Erlebacher, Stabilized nanoporous metals by dealloying ternary alloy precursors, *Adv. Mater.* 20 (2008) 4883-4886.
- [15] C.X. Xu, R.Y. Wang, M.W. Chen, Y. Zhang, Y. Ding, Dealloying to nanoporous Au/Pt alloys and their structure sensitive electrocatalytic properties, *Phys. Chem. Chem. Phys.* 12 (2010) 239-246.
- [16] Y. Yamauchi, Field-Induced alignment controls of one-dimensional mesochannels in mesoporous materials, *J. Ceram. Soc. Jpn.* 121 (2013) 831-840.
- [17] H. Wang, L. Wang, T. Sato, Y. Sakamoto, S. Tominaka, K. Miyasaka, N. Miyamoto, Y. Nemoto, O. Terasaki, Y. Yamauchi, Synthesis of mesoporous Pt films with tunable pore sizes from aqueous surfactant solutions, *Chem. Mater.* 24 (2012) 1591-1598.
- [18] L. Wang, Y. Yamauchi, Metallic nanocages: synthesis of bimetallic Pt-Pd hollow nanoparticles with dendritic shells by selective chemical etching, *J. Am. Chem. Soc.* 135 (2013) 16762-16765.
- [19] Y. Yamauchi, A. Tonegawa, M. Komatsu, H. Wang, L. Wang, Y. Nemoto, N. Suzuki, K. Kuroda, Electrochemical synthesis of mesoporous Pt-Au binary alloys with tunable compositions for enhancement of electrochemical performance, *J. Am. Chem. Soc.* 134 (2012) 5100-5109.

- [20] H. Atae-Esfahani, L.Wang, Y. Nemoto, Y. Yamauchi, Synthesis of bimetallic Au@Pt nanoparticles with Au core and nanostructured Pt shell toward highly active electrocatalysts, *Chem. Mater.* 22 (2010) 6310-6318.
- [21] H.J. Qiu, J.Q. Wang, P. Liu, Y. Wang, M.W. Chen, Hierarchical nanoporous metal/metal-oxide composite by dealloying metallic glass for high-performance energy storage, *Corros. Sci.* 96 (2015) 196-202.
- [22] Z.H. Zhang, Y. Wang, X.G. Wang, Nanoporous bimetallic Pt-Au alloy nanocomposites with superior catalytic activity towards electro-oxidation of methanol and formic acid, *Nanoscale* 3 (2011) 1663-1674.
- [23] J.L. Xu, C. Zhang, X.G. Wang, H. Ji, C.C. Zhao, Y. Wang, Z.H. Zhang, Fabrication of bi-modal nanoporous bimetallic Pt-Au alloy with excellent electrocatalytic performance towards formic acid oxidation, *Green Chem.* 13 (2011) 1914-1922.
- [24] S. Park, Y. Xie, M.J. Weaver, Electrocatalytic pathways on carbon-supported platinum nanoparticles: comparison of particle-size-dependent rates of methanol, formic acid, and formaldehyde, *Langmuir* 18 (2002) 5792-5798.
- [25] X.B. Ge, X.L. Yan, R.Y. Wang, F. Tian, Y. Ding, Tailoring the structure and property of Pt-decorated nanoporous gold by thermal annealing, *J. Phys. Chem. C* 113 (2009) 7379-7384.
- [26] A. Habrioux, W. Vogel, M. Guinel, L. Guetaz, K. Servat, B. Kokoh, N. Alonso-Vante, Structural and electrochemical studies of Au-Pt nanoalloys, *Phys. Chem. Chem. Phys.* 11 (2009) 3573-3579.

- [27] M.C. Dixon, T.A. Daniel, M. Hieda, D.M. Smilgies, M.H.W. Chan, D.L. Allara, Preparation, structure, and optical properties of nanoporous gold thin films, *Langmuir* 23 (2007) 2414-2422.
- [28] Y. Xia, J. Liu, W. Huang, Z.L. Li, Electrochemical fabrication of clean dendritic Au supported Pt clusters for electrocatalytic oxidation of formic acid, *Electrochimica Acta* 70 (2012) 304-312.
- [29] F. Xiao, Z.R. Mo, F.Q. Zhao, B.Z. Zeng, Ultrasonic-electrodeposition of gold-platinum alloy nanoparticles on multi-walled carbon nanotube-ionic liquid composite film and their electrocatalysis towards the oxidation of nitrite, *Electrochem. Commun.* 10 (2008) 1740-1743.
- [30] L.Y. Zhao, J.P. Thomas, N.F. Heinig, M. Abd-Ellah, X.Y. Wang, K.T. Leung, Au-Pt alloy nanocatalysts for electro-oxidation of methanol and their application for fast-response non-enzymatic alcohol sensing, *J. Mater. Chem. C* 2 (2014) 2707-2714.
- [31] F. Tao, M.E. Grass, Y. Zhang, D. R. Butcher, J. R. Renzas, Z. Liu, J.Y. Chung, B.S. Mun, M. Salmeron, G.A. Somorjai, Reaction-driven restructuring of Rh-Pd and Pt-Pd core-shell nanoparticles, *Science* 322 (2008) 932-934.
- [32] J. Luo, P.N. Njoki, Y. Lin, L.Y. Wang, Activity-composition correlation of AuPt alloy nanoparticle catalysts in electrocatalytic reduction of oxygen, *Electrochem. Commun.* 8 (2006) 581-587.
- [33] B.N. Wanjala, J. Luo, R. Loukrakpam, B. Fang, D. Mott, P.N. Njoki, M. Engelhard, H. R. Naslund, J.K. Wu, L.C. Wang, O. Malis, C.J. Zhong, Nanoscale alloying,

phase-segregation, and core-shell evolution of gold-platinum nanoparticles and their electrocatalytic effect on oxygen reduction reaction, *Chem. Mater.* 22 (2010) 4282-4294.

[34] B.D. Chandler, A.B. Schabel, L.H. Pignolet, Ensemble size effects on toluene hydrogenation and hydrogen chemisorption by supported bimetallic particle catalysts, *J. Phys. Chem. B* 105 (2001) 149-155.

[35] I. Banerjee, V. Kumaran, V. Santhanam, Synthesis and characterization of Au@ Pt nanoparticles with ultrathin platinum overlayers, *J. Phys. Chem. C* 119 (2015) 5982-5987.

[36] Z.G. Guo, X. Zhang, H. Sun, X.P. Dai, Y. Yang, X.S. Li, T.T. Meng, Novel honeycomb nanosphere Au@ Pt bimetallic nanostructure as a high performance electrocatalyst for methanol and formic acid oxidation, *Electrochim. Acta* 134 (2014) 411-417.

[37] Z. Liu, L. Hong, M.P. Tham, T.H. Lim, H.X. Jiang, Nanostructured Pt/C and Pd/C catalysts for direct formic acid fuel cells, *J. Power Sources*, 161 (2006) 831-835.

[38] Z.M. Peng, H. Yang, PtAu bimetallic heteronanostructures made by post-synthesis modification of Pt-on-Au nanoparticles, *Nano Research* 2 (2009) 406-415.

[39] N. Kristian, Y.S. Yan, X. Wang, Highly efficient submonolayer Pt-decorated Au nano-catalysts for formic acid oxidation, *Chem. Commun.* (2008) 353-355.

[40] D.N. Oko, J.M. Zhang, S. Garbarino, M. Chaker, D.L. Ma, A. C. Tavares, D. Guay, Formic acid electro-oxidation at PtAu alloyed nanoparticles synthesized by pulsed laser ablation in liquids, *J. Power Sources* 248 (2014) 273-282.

- [41] R.Y. Wang, C. Wang, W.B. Cai, Y. Ding, Ultra-low Pt loading, high performance nanoporous electrocatalysts with nanoengineered surface structures, *Adv. Mater.* 22 (2010) 1845-1848.
- [42] X.B. Ge, R.Y. Wang, S.Z. Cui, F. Tian, L.Q. Xu, Y. Ding, Structure dependent electrooxidation of small organic molecules on Pt-decorated nanoporous gold membrane catalysts, *Electrochem. Commun.* 10 (2008) 1494-1497.
- [43] B.T. Qiao, A.Q. Wang, X.F. Yang, L.F. Allard, Z. Jiang, Y.T. Cui, J.Y. Liu, J. Li, T. Zhang, Single-atom catalysis of CO oxidation using Pt_1/FeO_x , *Nat. Chem.* 3 (2011) 634-641.
- [44] S.H. Sun, G.X. Zhang, N. Gauquelin, N. Chen, J.G. Zhou, S.L. Yang, W.F. Chen, X.B. Meng, D.S. Geng, M. N. Banis, R.Y. Li, S.Y. Ye, S. Knights, G. A. Botton, T.-K. Sham, X.L. Sun, *Sci. Rep.* 2 (2013) 1775.
- [45] J. Yang, C. Tian, L. Wang, H.G. Fu, An effective strategy for small-sized and highly-dispersed palladium nanoparticles supported on graphene with excellent performance for formic acid oxidation, *J. Mater. Chem. C* 21 (2011) 3384-3390.
- [46] T. Biegler, D.A.J. Rand, R. Woods, Limiting oxygen coverage on platinized platinum; relevance to determination of real platinum area by hydrogen adsorption, *J. Electroanal. Chem.* 29 (1971) 269-277.
- [47] R.G. Xie, M.Z. Chen, J.Q. Wang, S.J. Mei, Y. Pan, H.W. Gu, Facile synthesis of Au-Pt bimetallic nanocomplexes for direct oxidation of methanol and formic acid, *RSC Adv.* 5 (2015) 650-653.

- [48] F.L. Zheng, W.T. Wong, K.F. Yung, Facile design of Au@Pt core-shell nanostructures: Formation of Pt submonolayers with tunable coverage and their applications in electrocatalysis, *Nano Research* 7 (2014) 410-417.
- [49] D. Zhao, Y.H. Wang, B.Q. Xu, Pt flecks on colloidal Au (Pt $\wedge$ Au) as nanostructured anode catalysts for electrooxidation of formic acid, *J. Phys. Chem. C* 113 (2009) 20903-20911.
- [50] Z.C. Zhang, J. Hui, Z.C. Liu, X. Zhang, J. Zhuang, X. Wang, Glycine-mediated syntheses of Pt concave nanocubes with high-index {hk0} facets and their enhanced electrocatalytic activities, *Langmuir* 28 (2012) 14845-14848.
- [51] B. Lim, X. Lu, M. Jiang, P.H.C. Camargo, E.C. Cho, E.P. Lee, Y. Xia, Facile synthesis of highly faceted multioctahedral Pt nanocrystals through controlled overgrowth, *Nano Lett.* 8 (2008) 4043-4047.
- [52] J. Kim, C. Jung, C.K. Rhee, T.H. Lim, Electrocatalytic oxidation of formic acid and methanol on Pt deposits on Au (111), *Langmuir* 23 (2007) 10831-10836.
- [53] M. Yin, Y.J. Huang, Q. Lv, L. Liang, J.H. Liao, C.P. Liu, W. Xing, Improved direct electrooxidation of formic acid by increasing Au fraction on the surface of PtAu alloy catalyst with heat treatment, *Electrochim. Acta* 58 (2011) 6-11.
- [54] B. Du, Y. Tong, A coverage-dependent study of Pt spontaneously deposited onto Au and Ru surfaces: direct experimental evidence of the ensemble effect for methanol electro-oxidation on Pt, *J. Phys. Chem. B* 109 (2005) 17775-17780.

Captions of tables and figures

Fig. 1. XRD patterns of (a) master $\text{Au}_{1-x}\text{Pt}_x\text{Al}_3$ alloy samples and (b) as-dealloyed AuPt and Au. The inset in (b) is the comparison of (111) diffraction peaks for the as-dealloyed samples. The standard pattern of intermetallic Al_2Au (PDF # 17-0877), Au (PDF # 04-0784) and Pt (PDF # 04-0802) are attached for comparison.

Fig. 2. XPS spectra of the as-dealloyed AuPt samples: (a) Au 4f peaks; (b) Pt 4f peaks: Pt(0) (solid), Pt(II) (dash), Pt(IV) (dot).

Fig. 3. SEM images with different enlargement scales, TEM, and HRTEM images of $\text{Au}_{99.5}\text{Pt}_{0.5}$ (a1–a4), $\text{Au}_{99}\text{Pt}_1$ (b1–b4), $\text{Au}_{98}\text{Pt}_2$ (c1–c4) and $\text{Au}_{95}\text{Pt}_5$ (d1–d4), respectively. The inset in a3, b3, c3 and d3 shows the corresponding SAED pattern.

Fig. 4. CVs of np-AuPt alloys and np-Au in 0.5 M H_2SO_4 at a sweep rate of 50 mV s^{-1} , the black solid square shows the region of H_{upd} adsorption/desorption while the dotted square shows the region of reduction of Pt oxides.

Fig. 5. (a) CV of the commercial JM-Pt/C in 0.5 M H_2SO_4 + 0.5 M HCOOH solution at a sweep rate of 50 mV s^{-1} . (b) CVs of np-AuPt alloys in 0.5 M H_2SO_4 + 0.5 M HCOOH solution at a sweep rate of 50 mV s^{-1} . (c) The mass activity of LSV for the commercial JM-Pt/C and np-AuPt alloys, recorded in 0.5 M H_2SO_4 + 0.5 M HCOOH solution at a sweep rate of 50 mV s^{-1} . The inset in (c) is the enlarged region of commercial JM-Pt/C. (d) The specific activity of LSV, recorded in 0.5 M H_2SO_4 + 0.5 M HCOOH solution at a sweep rate of 50 mV s^{-1} .

Fig. 6. CO stripping curves of (a) the commercial JM-Pt/C and (b-e) np-AuPt alloys in 0.5 M H_2SO_4 at 50 mV s^{-1} . All currents are normalized to the geometrical areas of electrodes. The solid curves show the first sweep while the dotted curves show the subsequent sweeps upon removal of the CO.

Fig. 7. The chronoamperometric response of the commercial JM-Pt/C and np-AuPt alloys towards FAO, measured in 0.5 M H₂SO₄ + 0.5 M HCOOH solution under a constant potential of −0.315 V for 2000 s.

Table 1 Electrochemical parameters of the as-dealloyed np-AuPt alloys and the commercial JM-Pt/C.

Table 2 Comparison of the as-dealloyed np-AuPt alloys with the commercial JM-Pt/C and the previously reported AuPt nanocatalysts with respect to their activities for FAO.

Table 1 Electrochemical parameters of the as-dealloyed np-AuPt alloys and commercial JM-Pt/C.

sample	Pt _{ECSA} (m ² g ⁻¹)	Pt content (μg)
Au _{99.5} Pt _{0.5}	22.3	0.25
Au ₉₉ Pt ₁	26.7	0.5
Au ₉₈ Pt ₂	27.3	1.01
Au ₉₅ Pt ₅	31.1	2.48
Pt/C	42.6	8.25

Table 2 Comparison of the as-dealloyed np-AuPt alloys with the commercial JM-Pt/C and the previously reported AuPt nanocatalysts with respect to their activities for FAO.

Sample	Morphology	Preparation Methods	Current density in ECSA / at fixed potential (mA cm ⁻²)	Current density in mass / at fixed potential (A mg _{Pt} ⁻¹)	Refs.
Au@Pt	nano branches	hydrogen reduction ion adsorption	\	0.1371 (~0.3 V vs. SCE)	47
Au@Pt/CNTs	core-shell nanostructure	electrochemical reduction	~ 0.45 (~ 0.45 V vs. SCE)	\	48
Pt _{0.05} /Au/C	spherical shape	hydrogen reduction	0.04 (0.4 V vs. SCE)	0.9124 (0.4 V vs. SCE)	49
Au ₈₀ Pt ₂₀	nanoporous	dealloying method	1.6 (0.58 V vs. RHE)	\	15
Au ₄₀ Pt ₆₀	nanoporous	dealloying method	\	0.5608 (0.4 V vs. SCE)	22
Au ₄₀ Pt ₆₀	nanoporous	dealloying method	\	0.3206 (0.4 V vs. SCE)	23
Au@Pt	honeycomb nanosphere	seed mediated method	3.33 (0.25 V vs. SCE)	0.2349 (0.25 V vs. SCE)	36
Au_{99.5}Pt_{0.5}	nanoporous	dealloying method	10.23 (-0.315 V vs. MSE)	7.01 (-0.315 V vs. MSE)	This work
Au₉₉Pt₁	nanoporous	dealloying method	7.81 (-0.315 V vs. MSE)	5.92 (-0.315 V vs. MSE)	This work
Au_{99.5}Pt_{0.5}	nanoporous	dealloying method	6.09 (-0.315 V vs. MSE)	4.51 (-0.315 V vs. MSE)	This work
Au₉₅Pt₅	nanoporous	dealloying method	2.57 (-0.315 V vs. MSE)	4.95 (-0.315 V vs. MSE)	This work
Pt/C	\	Commercial	0.82 (-0.315 V vs. MSE)	0.062 (-0.315 V vs. MSE)	This work

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)