Some Aspects on the One-Pot Fabrication of Nanoporous Pd–Au Surface Films by Electrochemical Alloying/Dealloying of (Pd–Au)–Zn from a Chlorozincate Ionic Liquid

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ABSTRACT: The high thermal stability of the Lewis acidic ZnCl2-1-ethyl-3-methylimidazolium chloride ionic liquid enables the in situ fabrication of hierarchical nanostructured Pd–Au bimetallic surfaces via electrochemical alloying/dealloying of (PdAu)Zn on PdAu substrate in the ionic liquid. Nanostructured PdAu samples that consist of patterned cracks and ligaments are fabricated by using potential cycling method and constant-potential electrolysis method, respectively. The effects of working temperature and amounts of the deposited Zn on the morphology of the dealloyed (PdAu)Zn nanostructure are examined. The formation of the hierarchical nanostructure is a compromise between high-surface-diffusive Au and low-surface-diffusive Pd. Whereas Au in the alloy promotes the formation of the nanostructure, Pd in the PdAu nanostructure protects this material from coarsening. Compared with the plain PdAu, the nanostructured PdAu surface prepared at 150 °C exhibits a significantly higher active surface area and a high capability for the electro-oxidation of glucose.

INTRODUCTION

Micro- and nanoporous metal materials are useful for a wide variety of applications such as electrocatalysis, sensors, and others because of their high active surface area-to-volume ratio associated with their porous structure.1 Among the various methods developed for fabricating porous metals, dealloying has received great attention owing to its easy operation.1 In a dealloying process, the less-noble component of an alloy is selectively dissolved either chemically or electrochemically, resulting in a porous structure of the nobler component.2–4 The evolution of the porous structure during dealloying has been described in detail.5,6 The porosity evolution is a result of surface diffusion and reorganization of the noble metal at the dealloying interface and therefore is strongly associated with the surface diffusivity (mobility) of the respective alloy components; a higher metal surface diffusivity usually promotes the formation of pores. However, a high surface diffusivity also promotes the coarsening of the porous structure because porous metals are thermodynamically metastable and tend to reduce their surface energy via coarsening. As observed for the nanoporous gold material, coarsening may greatly reduce the usable lifetimes of the porous metals.5 One way to reduce coarsening is to add a slowly moving noble third component to the precursor alloy. As demonstrated by adding Pt to the Ag–Au alloy prior to dealloying, the lower Pt surface diffusivity successfully hinders coarsening.5,6

Most of the earlier studies of dealloying were focused on binary alloy systems, but recently ternary or multicomponent alloy systems such as Al–Pd–Au,8 Cu–Au–Pt,9 Ag–Au–Pt,8,10 and glassy Pd–Ni–Pt11,12 have attracted increasing attention for the fabrication of nanoporous materials. To date, most of the dealloying studies are performed using alloy precursors prepared by high-temperature thermal casting, followed by chemical etching in corrosive media. By contrast, electrochemical alloying and dealloying can be another approach for the fabrication of porous metals. For example, the electrodeposition of CuNi alloy in an aqueous electrolyte, followed by the electrochemical dissolution of Cu from the alloy, results in petal-like nanoporous Ni materials13,14 which are applied for electrocatalysis and energy storage devices. Furthermore, nanostructured metal materials have also been fabricated by the electrodeposition of Zn onto the metal surfaces such as Pt,15 Au,16 Ag,17 Cu,18,19 and Pd in an ambient-temperature ionic liquid,20 followed by the electrochemical dissolution of Zn under relatively mild conditions. The electrochemical alloying/dealloying approach could be a convenient and green-chemistry approach for fabricating nanostructured materials because the alloying process can be operated at a relatively low temperature compared to thermal casting and allow easy adjustment of the alloy composition and recycle of the dealloyed component. With electrochemical...
alloying/dealloying, bicontinuous nanoporous structures are obtained for relatively mobile metals such as Au, Ag, and Cu, but cracklike nanopatterned structures are obtained for less mobile metals such as Pt and Pd. Furthermore, it was found that to improve the formation of alloy during electrochemical alloying step, a moderate high temperature around 120–170 °C is beneficial. In this regard, ambient-temperature ionic liquid electrolytes appear to be more preferable than aqueous electrolytes because of their superior properties including high thermal stability, low vapor pressure, low flammability, and wide electrochemical window in comparison with conventional molecular solvents.

Although the electrochemical formation of binary alloys for the electrochemical dealloying fabrication of nanostructured materials has been reported, electrochemical alloying of ternary alloys for the electrochemical fabrication of nanostructured materials is less explored. In view of this, the nanostructured Pd–Au alloys are valuable materials for various applications. Herein, we report the fabrication of Pd–Au nanostructures by electrochemical alloying/dealloying of Zn on PdAu substrate in a Lewis acidic ZnCl2-1-ethyl-3-methylimidazolium chloride (40.0–60.0 mol % ZnCl2-EMIC) ionic liquid.

Two different electrochemical methods multiscan cyclic voltammetry and constant-potential electrolysis were compared for this purpose. In the multiscan cyclic voltammetric method, the potential of the PdAu substrate was cycled between a cathodic value and an anodic value. Zn was deposited on the PdAu substrate during the cathodic potential sweep and stripped off during the anodic potential sweep. The morphology of the resulted PdAu nanostructure was found to be dependent on the number of potential cycles. In the constant-potential electrolysis method, a certain amount of Zn was electrodeposited at a constant cathodic potential, followed by removing Zn at a constant anodic potential. The effects of the working temperature and amounts of the electrodeposited Zn on the evolution of the nanostructures were investigated. It was found that the constant-potential electrolysis method produced finer PdAu nanostructures than the multiscan cyclic voltammetric method. The presence of highly mobile Au facilitates the nanoligament formation. Meanwhile, the presence of less mobile Pd slows down the coarsening that could be resulted from the diffusion of Au. Therefore, hierarchical PdAu nanostructures containing both patterned cracks and nanoligaments were obtained. The prepared nanostructured PdAu appear to be a good electrode material for electrocatalytic reactions such as glucose electro-oxidation.

## RESULTS AND DISCUSSION

Typical cyclic voltammograms for the electrodeposition and stripping of Zn at various electrodes including polycrystalline glassy carbon, PdAu, Au, and Pd in the 40.0–60.0 mol % ZnCl2-EMIC ionic liquid at 150 °C are shown in Figure 1A. The voltammograms show that the reduction of Zn(II) on the GC starts at about −0.2 V, corresponding to the deposition of Zn, whereas the reduction process occurs at potentials less negative than −0.2 V on the PdAu, Au, and Pd substrates, indicating that less overpotential is required for the deposition of Zn on the metal substrates. This fact could be a result of the high work functions of Pd (5.2–5.6 eV) and Au (5.1–5.47 eV) in comparison to those of C (5 eV) and Zn (3.69–4.9 eV). A larger work function difference between the substrate and the deposits facilitates the reduction to occur. On the reverse potential sweep, only a single anodic peak (a1) due to the stripping of the Zn electrodeposits is observed on the GC electrode, whereas multiple stripping peaks (a1, a2) are observed on the metal electrodes, indicating the stripping of various surface alloy electrodeposits that were formed between the deposited Zn and the metal substrates. Note that the stripping peak a1 is due to the stripping of Zn-rich alloys on the top layers of the deposits and the stripping peaks a2–a3 resulted from the stripping of the alloys deeper in the substrates because a phase with a higher Pd and/or Au content would be oxidized at a more positive potential than that with a higher Zn content. The decrease of peak a2 and increase of peaks a3–a4 indicate the decrease of the amount of Zn deposits that remain on the top surface of the substrate and the increase of the amount of Zn alloys formed. In accordance with the higher atom diffusivity of Au than that of Pd, the relative intensities of these stripping peaks suggest that the ease of alloy formation follows the trend from Au–Zn > (PdAu)–Zn > Pd–Zn. The temperature effects on the formation of Zn alloys on the PdAu substrate are further illustrated in Figure 1B, with the cyclic voltammograms recorded for the electrodeposition and stripping of Zn on a polycrystalline PdAu substrate in the 40.0–60.0 mol % ZnCl2-EMIC ionic liquid at various temperatures from 90 to 150 °C. As shown, because the
viscosity of the electrolyte decreases and therefore the mass transport of the Zn(II) species to the electrode surface increases with increasing temperature, the reduction current increases with increasing temperature, reflecting the more facile deposition of Zn at higher temperature. Meanwhile, the voltammogram recorded at 90 °C shows only a single stripping peak a1, indicating that the deposited Zn does not effectively alloy with the PdAu substrate at this temperature. When the temperature was increased to 110 and 130 °C, peak a1 increased as more Zn was deposited during the cathodic scan, meanwhile peak a2 also increased because the efficiency of the (PdAu)Zn alloy formation was increased. Moreover, substantial increase in peak a3 and decrease in peak a4 are observed at 150 °C because substantial amounts of the deposited Zn had alloyed with PdAu and the relative amounts of unalloyed Zn became less. These facts indicate that a higher temperature is necessary for the effective formation of the (PdAu)Zn surface alloy. This can be attributed to the accelerated interdiffusion of Zn and PdAu with increasing temperature.

The cyclic voltammograms that are shown in Figure 1 suggest that the electrochemical formation of (PdAu)Zn surface alloys is possible. The electrochemical formation of (PdAu)Zn surface was studied by the constant-potential electrodeposition of 10 C cm−2 of Zn at −0.2 V onto the PdAu substrate from the 60.0 mol % ZnCl2-EMIC liquid at 150 °C. To enhance the formation of the (PdAu)Zn alloys, the Zn-deposited samples were kept in the solution for 1 h after each electrodeposition experiment to let the deposited Zn diffuse into the PdAu substrate. The as-deposited samples were cleaned by washing off the residual melt and characterized with X-ray diffraction (XRD). Shown in Figure 2 are the XRD patterns for the Zn-deposited PdAu samples prepared at various temperatures from 90 to 150 °C.

![XRD patterns](image)

Figure 2. XRD patterns (Cu Kα) of the PdAu samples deposited with 10 C cm−2 of Zn from the ZnCl2-EMIC ionic liquid at various temperatures from 90 to 150 °C.

and 75.18°. The intensity of the (PdAu)Zn diffractions increases with increasing temperature while the diffractions due to Zn and PdAu decrease with increasing temperature, indicating that the formation of (PdAu)Zn requires a sufficient high temperature to facilitate the interdiffusion of the deposited Zn and the PdAu substrate. It should be noted that no significant interdiffusion of the deposited Zn and the PdAu substrate was observed when the Zn-deposited PdAu was immersed in the melt solution at room temperature for a time period longer than 24 h. The cyclic voltammograms shown in Figure 1 imply that although (PdAu)Zn alloy can be formed by deposition at −0.2 V, it is possible to dealloy the (PdAu)Zn surface alloy by the selective anodic dissolution of Zn at 1.0 V to produce porous PdAu. Therefore, the preparation of the porous PdAu was investigated by the constant-potential deposition of Zn at −0.2 V to form the (PdAu)Zn surface, followed by the dissolution of Zn from the (PdAu)Zn at 1.0 V.

The effect of temperature on the morphology of the as-produced PdAu surface is illustrated in Figure 3, with the scanning electron microscopy (SEM) micrographs recorded for the PdAu samples prepared at various temperatures (90, 110, 130, and 150 °C) by the deposition of 10 C cm−2 (5.18 × 10−5 mol cm−3) Zn, followed by dissolving the deposited Zn at −1.0 V. As shown in Figure 3A, only shallow cracks are produced on the PdAu sample prepared at 90 °C. The SEM image shown in Figure 3B reveals that the number and depth of the cracks increased when the temperature was increased to 110 °C. Figure 3C shows that when the temperature was increased to 130 °C, the width and depth of the cracks further increased and some fine structures (such as secondary cracks) appeared on the islands separated by the cracks. As shown in Figure 3D, when the preparation temperature was further increased to 150 °C, dramatic morphology evolution is observed on the PdAu sample because nanostructures composed of ligament aggregates are apparent on the islands separated by the wide and deep cracks. These results can be understood as the diffusion rate of the metal atoms is slow at low temperature so that the deposited Zn atoms do not diffuse well into the PdAu and alloying reaction does not occur to an appreciable extent during the deposition step and thus the diffusion of Zn atoms is unable to produce significant morphology change during the dissolution step. On the other hand, the interdiffusion of the metal atoms increases with increasing temperature and more of the deposited Zn atoms could alloy with PdAu atoms, resulting in more significant volume change in the alloy during the deposition step, thus producing more pronounced morphology changes, and creating a porous PdAu surface after the Zn atoms are selectively dealloyed. Among the temperatures examined, the temperature of 150 °C apparently gives the best morphology. The coexistence of cracks and ligaments on the dealloyed PdAu can be attributed to the different diffusivities of Pd and Au.52 The low diffusivity of Pd predominantly results in the cracks, whereas the high diffusivity of Au governs the formation of ligaments. The microstructure of porous PdAu materials produced from dealloying of the (PdAu)Zn is dependent on the alloy composition, which can be varied by the amount of deposited Zn. A series of porous PdAu samples were prepared at 150 °C by the deposition of different amounts of Zn at −0.2 V, followed by selective dealloying at +1.0 V. The SEM images of these porous PdAu samples are shown in Figure 4. As can be seen in Figure 4A, the (PdAu)Zn alloy film formed is thin and no obvious changes in the surface morphology are observed when the amount of the deposited Zn is as low as 1 C.
On the other hand, as shown in Figure 4B, cracks and pores started to appear in the dealloyed PdAu sample that had been deposited with a higher quantity (5 C cm$^{-2}$) of Zn because the (PdAu)Zn was thicker and higher in Zn content. Finally, Figures 4C and 3D show that further increasing the thickness and Zn content of the (PdAu)Zn alloy film by increasing the deposited Zn amount to 10 C cm$^{-2}$ brought in a significant change in the morphology; both deep cracks and islands made of nanometer-sized ligaments are present.

Porous Pd and porous Au samples were also prepared at 150 °C by depositing 10 C cm$^{-2}$ of Zn, followed by dealloying at +1.0 V. The SEM images of the dealloyed Pd, Au, and PdAu samples are presented in Figure 5. The SEM image shown in Figure 5A reveals that the Pd sample prepared under this condition had a smooth surface with a few isolated pores. The Au sample, on the other hand, exhibited a rough surface with numerous small pores, while the PdAu sample showed a combination of both features, with a significant number of deep cracks and islands.
condition displays primarily rough islands separated by cracks having a width of about 200 nm. Meanwhile, Figure 5B indicates that the Au sample surface is composed of severely coarsened ligaments. By contrast, Figure 5C shows that fine nanostructures are obtained with PdAu. The different morphologies can be attributed to the different diffusivities of these materials. The low diffusivity of Pd makes it difficult for Zn to diffuse into the Pd sample during the deposition step and difficult for the reconstruction of the surface during the dealloying step, leading to the cracks. Apparently, a temperature higher than 150 °C is required for the preparation of fine porous Pd. The high diffusivity of Au makes it easy for both the formation of the surface AuZn alloy during the deposition step and the reconstruction of the surface during the dealloying step. However, the high diffusivity of Au also causes serious coarsening. It is known that nanoporous Au composed of interconnected ligaments can be prepared at temperatures below 120 °C.26 For the PdAu sample, the low diffusivity of Pd minimizes the coarsening while the high diffusivity of Au facilitates the formation of nanostructures containing micrometer pores and nanometer ligaments during dealloying of (PdAu)Zn. The above results indicate that the morphology of the porous PdAu prepared by the constant-potential deposition of Zn, followed by the selective anodic dissolution of the

Figure 6. Multiple scan cyclic voltammograms recorded at a scan rate of 10 mV s⁻¹ for electrochemical alloying/dealloying of (PdAu)Zn at (A) 120 and (B) 150 °C in the 40.0–60.0 mol % ZnCl₂-EMIC melt. SEM images of the PdAu samples prepared at (C) 120 and (D) 150 °C with a potential cycle number of 30.

Figure 7. SEM images of the PdAu samples prepared at 150 °C by multiple potential scan between −0.3 and 1.0 V in the 40.0–60.0 mol % ZnCl₂-EMIC melt. The number of potential cycles is (A) 15, (B) 20, (C) 25, and (D) 30.
purposes of the metal atoms. An alternative way to prepare porous PdAu using the electrochemical alloying/dealloying approach is by cycling the potential of the PdAu electrode between −0.3 and 1.0 V. It is expected that Zn is deposited on the PdAu and forms (PdAu)Zn during the cathodic potential sweep and dealloyed from the (PdAu)Zn alloy during the anodic potential sweep to produce porous PdAu. The multiple scan cyclic voltammograms recorded at a scan rate of 10 mV s−1 for electrochemical alloying/dealloying of (PdAu)Zn at 120 and 150 °C, respectively, in the 40.0–60.0 mol % ZnCl2-EMIC melt are presented in Figure 6. In these voltammograms, the anodic peak a1 is attributed to the stripping of bulk Zn deposit, whereas the anodic peak a2 is attributed to the stripping of Zn of the (PdAu)Zn. As shown in Figure 6A, no noticeable changes are observed in the voltammogram recorded at 120 °C; the stripping peak a1 remains higher than the stripping peak a2, indicating that no appreciable (PdAu)Zn was formed during the cathodic potential scan. On the other hand, Figure 6B shows obvious changes in the voltammogram recorded at 150 °C; the anodic peak a1 decreases while the anodic peak a2 increases with increasing cycling number, indicating the formation of (PdAu)Zn. However, no further alteration in these voltammograms is observed when the potential cycle number is higher than 20, suggesting that a steady state is reached. The SEM images recorded for the PdAu samples prepared at 120 and 150 °C, respectively, with a potential cycle number of 30 are given in Figure 6C,D. It is apparent that the PdAu sample prepared at 150 °C exhibits a better defined porous structure than that prepared at 120 °C. The effect of the number of potential cycles on the prepared PdAu samples is illustrated by the SEM images shown in Figure 7. This figure clearly shows that the PdAu nanostructures developed with increasing potential cycle number. Although porous PdAu materials could be prepared by both constant-potential alloying/dealloying and potential cycling approaches, their final porous structures are different. The former approach produced porous PdAu samples that consist of cracks and islands formed by nanoligaments, whereas the latter approach produced porous PdAu samples that consist of cracks and islands having small holes. This may be resulted from the more efficient coarsening process associated with the latter approach. Coarsening proceeded to reduce the surface energy once the alloy is dealloyed. Because, in the potential cycling approach, there was only a limited time for the formation of a thin (PdAu)Zn surface alloy layer during each cathodic potential scan and only a limited porous PdAu layer was produced during the anodic dealloying potential scan, the coarsening process of the thin-layer nanostructure is more efficient. Although subsequent potential scans thickened the porous PdAu layer, the highly mobile Au content in the porous PdAu continuously promoted the coarsening of the structure during each potential cycle, leading to a significant increase of the PdAu “ligament” size. Therefore, the fine structures are lost, leaving small holes.

Cyclic voltammograms recorded on the plain PdAu and porous PdAu electrodes prepared with constant-potential alloying/dealloying (denoted as PdAuCP) and potential cycling (denoted as PdAuCV) in a 0.1 M NaOH aqueous solution and (B) voltammograms recorded on the PdAuCP in a 0.1 M NaOH solution with and without 20 mM glucose. The temperature was 30 °C with a potential scan rate of 50 mV s−1.

Figure 8. (A) Cyclic voltammograms recorded on the plain PdAu and porous PdAu electrodes prepared with constant-potential alloying/dealloying (denoted as PdAuCV) and potential cycling (denoted as PdAuCP) in a 0.1 M NaOH aqueous solution and (B) voltammograms recorded on the PdAuCP in a 0.1 M NaOH solution with and without 20 mM glucose. The temperature was 30 °C with a potential scan rate of 50 mV s−1.

metal hydroxide, and the formation of metal oxides, respectively, whereas the cathodic peaks c1, c2, and c3 are due to the cathodic adsorption of hydrogen, reduction of Pd oxide, and reduction of Au oxide, respectively. It appears that the porous PdAuCP gives much higher peak currents than the PdAuCV and plain PdAu. The charges integrated from the current under the peaks c2 and c1 of these voltammograms give a ratio following the trend of PdAuCP (19.8 mC) > PdAuCV (2.22 mC) > plain PdAu (0.32 mC). This indicates that with the same geometric area, the PdAuCP electrode exhibits an active surface area about 66 times higher than that of the plain PdAu electrode. Therefore, the porous PdAuCP electrode that was prepared by the constant-potential deposition of 10 C cm−2 of Zn at −0.2 V followed by dealloying at 1.0 V in the 40.0–60.0 mol % ZnCl2-EMIC melt at 150 °C was tested for the electrochemical detection of glucose in aqueous solution. Typical cyclic voltammograms recorded on the PdAuCP at 30 °C in a 0.1 M NaOH solution with and without 20 mM glucose are shown in Figure 8B. Judging against these two voltammograms, it is apparent that the current peak at about 0.0 V is due to the oxidation of glucose and can be used for the detection of glucose. The performance of the PdAuCP electrode toward the detection of glucose was investigated using an amperometric method. The current responses of the PdAuCP electrode at deposited Zn, can be manipulated by the operating temperature and the amounts of deposited Zn. The final morphology is also strongly affected by the diffusivity of the metal atoms. An alternative way to prepare porous PdAu using the electrochemical alloying/dealloying approach is by cycling the potential of the PdAu electrode between −0.3 and 1.0 V. It is expected that Zn is deposited on the PdAu and forms (PdAu)Zn during the cathodic potential sweep and dealloyed from the (PdAu)Zn alloy during the anodic potential sweep to produce porous PdAu. The multiple scan cyclic voltammograms recorded at a scan rate of 10 mV s−1 for electrochemical alloying/dealloying of (PdAu)Zn at 120 and 150 °C, respectively, in the 40.0–60.0 mol % ZnCl2-EMIC melt are presented in Figure 6. In these voltammograms, the anodic peak a1 is attributed to the stripping of bulk Zn deposit, whereas the anodic peak a2 is attributed to the stripping of Zn of the (PdAu)Zn. As shown in Figure 6A, no noticeable changes are observed in the voltammogram recorded at 120 °C; the stripping peak a1 remains higher than the stripping peak a2, indicating that no appreciable (PdAu)Zn was formed during the cathodic potential scan. On the other hand, Figure 6B shows obvious changes in the voltammogram recorded at 150 °C; the anodic peak a1 decreases while the anodic peak a2 increases with increasing cycling number, indicating the formation of (PdAu)Zn. However, no further alteration in these voltammograms is observed when the potential cycle number is higher than 20, suggesting that a steady state is reached. The SEM images recorded for the PdAu samples prepared at 120 and 150 °C, respectively, with a potential cycle number of 30 are given in Figure 6C,D. It is apparent that the PdAu sample prepared at 150 °C exhibits a better defined porous structure than that prepared at 120 °C. The effect of the number of potential cycles on the prepared PdAu samples is illustrated by the SEM images shown in Figure 7. This figure clearly shows that the PdAu nanostructures developed with increasing potential cycle number. Although porous PdAu materials could be prepared by both constant-potential alloying/dealloying and potential cycling approaches, their final porous structures are different. The former approach produced porous PdAu samples that consist of cracks and islands formed by nanoligaments, whereas the latter approach produced porous PdAu samples that consist of cracks and islands having small holes. This may be resulted from the more efficient coarsening process associated with the latter approach. Coarsening proceeded to reduce the surface energy once the alloy is dealloyed. Because, in the potential cycling approach, there was only a limited time for the formation of a thin (PdAu)Zn surface alloy layer during each cathodic potential scan and only a limited porous PdAu layer was produced during the anodic dealloying potential scan, the coarsening process of the thin-layer nanostructure is more efficient. Although subsequent potential scans thickened the porous PdAu layer, the highly mobile Au content in the porous PdAu continuously promoted the coarsening of the structure during each potential cycle, leading to a significant increase of the PdAu “ligament” size. Therefore, the fine structures are lost, leaving small holes.

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−0.08 V to a series addition of glucose into a 1.0 M NaOH solution are shown in Figure 9A. As illustrated in this figure, the response current of the PdAuCP electrode was found to increase abruptly to a steady-state value upon each addition of glucose with a quick response time of ca. 5 s. A calibration curve constructed for the detection of glucose using this electrode is shown in Figure 9B. As can be seen, the calibration curve is linear in the range of 1−14 mM glucose with a correlation coefficient of 0.999 and a sensitivity of 2.65 mA cm⁻² mM⁻¹, indicating that the PdAuCP prepared in this study is potentially useful for the electro-oxidation of glucose.

The stability of the PdAuCP electrode was examined by cycling the electrode between −1.0 and 0.8 V in a 1.0 M NaOH solution. The surface morphology of a PdAuCP electrode and a nanoporous Au electrode after 1000 potential cycles was examined with SEM. As shown in Figure 10, the PdAuCP electrode exhibits much less changes in the morphology in comparison with that of the nanoporous Au electrode. The less change in the morphology of the PdAuCP electrode apparently proves that because of the lower diffusivity of Pd, the PdAuCP is less prone to coarsening and is able to preserve its nanostructure with respect to that of the more mobile pure porous Au during the potential cycles. Moreover, no appreciable alteration was observed in the cyclic voltammograms recorded on the PdAuCP after 1000 cycles, indicating that the PdAuCP electrode is more stable.

CONCLUSIONS

The one-pot fabrication of nanoporous PdAu films through electrochemical alloying/dealloying was examined in a Lewis acidic ZnCl₂-EMIC ionic liquid. The formation of the hierarchical nanostructure is realized as a result of the high surface diffusivity of Au, which facilitated the formation of ligaments, and the low surface diffusivity of Pd, which prevented the coarsening of the porous structures. The fabrication was performed by the electrodeposition of certain amounts of Zn onto the PdAu substrate to form the (PdAu)Zn surface alloy, followed by the selective anodic dissolution of Zn from the surface alloy. For comparison, the preparation of the PdAu nanostructure was also carried out by multiple scan potential cycling. It is found that the morphology of the produced PdAu nanostructure is greatly affected by the working

Figure 9. (A) Current responses of the PdAuCP electrode at −0.08 V to a series addition of glucose into a 1.0 M NaOH solution and (B) the calibration curve constructed for the detection of glucose using the data taken from (A).

Figure 10. SEM images of the porous (A,B) PdAuCP and (C,D) AuCP electrodes before (A,C) and after (B,D) 1000 potential cycles between −1.0 and 0.8 V in a 1.0 M NaOH solution.
temperature. A high temperature favored alloying/dealloying but also enhanced the coarsening of the porous structure. Moreover, the results indicated that the PdAu porous films prepared with constant-potential electrolysis were thicker and provide higher electrochemical active surface area than those prepared with the multiple potential cycling. The porous PdAu films prepared by the deposition and dissolution of 10 C cm$^{-2}$ Zn at 150 °C showed an excellent performance for the electro-oxidation of glucose in alkaline aqueous solution.

Overall, the results demonstrated that by taking the advantage of the high thermal stability of the ZnCl$_2$-EMIC ionic liquid, electrochemical alloying/dealloying can be applied to the fabrication of bimetallic or multicomponent porous materials containing less mobile metal components. It should be pointed out that the crack-ligament-mixed morphologies resulted from electrochemical alloying/dealloying are different from the bicontinuous porous structure prepared from the thermal-casting alloying and chemical dealloying methods. Because the final nanostructure is a compromise between high-diffusive Au and low-diffusive Pd, varying the composition of the original PdAu substrate should also affect the procedure and the final nanostructures. It should be noted that although this work was conducted in a glovebox, it is very likely that similar results can be obtained when the electrochemical alloying/dealloying fabrication of the porous materials was conducted in air. These aspects will be further studied.

**EXPERIMENTAL SECTION**

EMIC (Aldrich) was prepared and purified according to the method described in the literature.$^{46}$ A colorless ZnCl$_2$-EMIC (40.0–60.0 mol %) ionic liquid was prepared by mixing proper amounts of ZnCl$_2$ (Aldrich, 98%) and EMIC at 90 °C for 6 h in a N$_2$-filled glovebox (vacuum atmosphere). The electrochemical alloying/dealloying fabrication of the porous PdAu was conducted in the N$_2$-filled glovebox. The electrochemical experiments were conducted with an Autolab 302N potentiostat/galvanostat controlled with the GPES software. A three-electrode electrochemical cell was used for all electrochemical experiments. The counter electrode was a Zn (Aldrich, 99.9%) spiral immersed in the pure 40.0–60.0 mol % ZnCl$_2$-EMIC liquid contained in a frittled glass tube, and the reference electrode was also a Zn wire (Aldrich, 99.9%) placed in a separated frittled glass tube containing pure 60–40 mol % ZnCl$_2$-EMIC ionic liquid. For cost reason, the experiments for the fabrication of nanostructured PdAu were conducted at PdAu wires (Pd/Au; 40/60 wt %, Alfa Aesar, 99.9%, diameter = 0.2 mm). The polished PdAu wire working electrode was first degreased in acetone, followed by immersion in 2 M HNO$_3$(aq), rinsed with deionized water, and dried before use. To fabricate the nanostructured PdAu electrode, (PdAu) Zn surface alloys were first formed by the electrodeposition of Zn at the PdAu wire in the 40.0–60.0 mol % ZnCl$_2$-EMIC ionic liquid. Zn in the (PdAu)Zn surface alloys was then anodically stripped off to create the nanostructured surface. For comparison, the preparation of nanostructured Pd (99.9%, 0.5 mm in diameter) wires and Au (99.9%, 0.2 mm in diameter) wires was also conducted with the same procedure. The microstructure of the electrode was examined with a high-resolution scanning electron microscope (ZEISS AURIGA FE-SEM) and energy-dispersive X-ray spectroscopy. The crystalline phases of the deposits on the PdAu wires were examined with a Shimadzu XD-D1 X-ray diffractometer.

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**Notes**

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