SECM Screening of the Catalytic Activities of AuPd Bimetallic Patterns Fabricated by
Electrochemical Wet-Stamping Technique

Mengwei Ye^a, Yi Li^{b,*}, Juan Wu^b, Tongyu Su^a, Jie Zhang^c, Jing Tang^{a,*}

^a *Key Laboratory of Analysis and Detection Technology for Food Safety, Ministry of Education, College of Chemistry, Fuzhou University, Fuzhou, 350108, Fujian Province, P. R. China;*

^b *College of Chemistry, Fuzhou University, Fuzhou, 350108, Fujian Province, P. R. China;*

^c *State Key Laboratory for Physical Chemistry of Solid Surfaces, and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, Fujian Province, P. R. China*

* Corresponding author.

Telephone and fax numbers: +86 591 22866165, +86 591 22866155

E-mail address: jingtang@fzu.edu.cn, liy99@fzu.edu.cn

Abstract

Electrocatalyst arrays with various AuPd compositions have been deposited onto an indium tin oxide (ITO) surface by an electrochemical wet-stamping (EWETS) technique. Micropatterned high-strength agarose containing different solutions of chloroauric acid and chloropalladic acid has been used to electrodeposit and generate patterns of AuPd nanoparticle arrays on ITO. The compositions of the AuPd catalysts prepared by EWETS have been determined through a combination of energy-dispersive X-ray analysis (EDX) and X-ray diffraction spectroscopy (XRD). Field-emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) have been employed to characterize their morphology. The electrochemical activities of the AuPd alloys for H_2O_2 and FcMeOH^+ reduction reactions have been investigated in both redox-competition and feedback modes by means of scanning electrochemical microscopy (SECM). The results obtained from SECM images were well corroborated by calculated heterogeneous electron transfer (HET) rates for the respective AuPd electrodes, demonstrating that the SECM was applicable for the screening of multicomponent alloy catalysts and determining the optimal composition for electrocatalytic reactions.

KeyWords: Agarose stamp; AuPd bimetallic nanoparticles; Electrochemical wet-stamping; Redox-competition mode; Scanning electrochemical microscopy

1. Introduction

Recently, AuPd bimetal nanoparticles exhibit high electrocatalytic activity and particularly effective for the direct synthesis of hydrogen peroxide and the oxidation of alcohols. To assess the influence of the compositions of AuPd co-deposits on their catalytic properties, a variety of screening tools, such as scanning electrochemical microscopy (SECM) [1], fourier-transform infrared imaging [2], fluorescence imaging[3], electrochemiluminescence imaging [4], and molecular magnetic resonance imaging[5], have been used. SECM has been proved as a good technique for evaluating the local electrocatalytic activity of different catalysts [6-8] and also represents a powerful electrochemical tool for investigating heterogeneous electron-transfer (HET) reactions at interfaces between an electrode and an electrolyte[9]. For example, it has been applied in detection and quantification of H_2O_2 [10-13], which not only is an important species in energy storage field such as intermediate of oxygen reduction reaction[14-17] but also plays an important role in clinical applications, and environmental analysis. The redox-competition mode (RC) of SECM has been applied for screening of the electrocatalysts in the reduction of H_2O_2 by Schuhmann and co-workers[18-22]. Moreover, the preparation of electrocatalysts with different defined compositions is still challenging. Bard and co-workers[23-27] prepared catalyst spots consisting of mixtures of different metals arranged in high-density arrays on glassy carbon (GC) by reduction of metal salt precursors with sodium borohydride or hydrogen. Schuhmann et al. [18, 19, 28] used a droplet cell to deposit PdPt and PdAu

catalyst spots of different compositions on graphite discs. Both of these techniques are not efficient to prepare the alloy patterns and the typical pattern is circle. In previous years, our group [29-31] has proposed a simple method, referred to as electrochemical wet-stamping (EWETS), which relies on a microstructured agarose stamp containing a solution, which is employed to electrodeposit and generate array patterns efficiently and rapidly. This method can be employed to deposit AuPd alloy patterns with different compositions by varying the electrodeposition conditions, such as the electrolyte composition, current density, and applied potential.

Herein, we describe application of the electrochemical wet-stamping technology to fabricate patterns made of AuPd alloy NPs on ITO. The surface morphologies and compositions of the AuPd NPs comprising the microfabricated patterns produced by EWETS have been characterized by field-emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM), and their compositions have been studied through a combination of energy-dispersive X-ray analysis (EDX) and X-ray diffraction spectroscopy (XRD). Cyclic voltammetry has been carried out to examine the electrochemical activity of the AuPd catalysts. Furthermore, the redox-competition mode (RC) of SECM has been applied for screening of the electrocatalysts in the reduction of H_2O_2 . Feedback and generation/collection (G/C) modes have been used to study the electron transfer reaction in reduction of FcMeOH^+ and the HET rate of the reduction reaction that was determined by comparison of SECM feedback approach curves with Comsol Multiphysics simulations.

2. Experimental Methods

2.1. Preparation of the AuPd Electrodes.

Indium tin oxide (ITO) with a surface resistance of $30 \Omega \cdot \text{cm}^{-1}$, purchased from Xiamen ITO Photoelectricity Industry Corporation, was used as the working electrode. The ITO substrate was cut into pieces of $15 \text{ mm} \times 20 \text{ mm}$ and then ultrasonically cleaned with acetone, ethanol, and ultrapure water in sequence and then thoroughly dried under a stream of nitrogen. Chloroauric acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), palladium chloride (PdCl_2), hydrochloric acid (HCl), sodium sulfate (Na_2SO_4), and hydrogen peroxide (H_2O_2) were purchased from Sinopharm Chemical Corporation. Chloropalladic acid (H_2PdCl_4) was prepared from palladium chloride and hydrochloric acid (3:1). All of the chemicals were of analytical grade. Reagent solutions were prepared using Milli-Q water.

AuPd NP arrays with different compositions were prepared on ITO electrodes according to the procedure illustrated in Fig. 1. Micropatterned agarose stamps were prepared according to the procedure published previously[32]. Three kinds of electrolytes containing mixed salts were employed in the experiments. The simplified forms are denoted as follows. $0.75 \text{ mmol} \cdot \text{L}^{-1} \text{HAuCl}_4$ and $0.25 \text{ mmol} \cdot \text{L}^{-1} \text{H}_2\text{PdCl}_4$ and $0.1 \text{ mol} \cdot \text{L}^{-1} \text{KCl}$ ($C_{\text{HAuCl}_4}:C_{\text{H}_2\text{PdCl}_4}=3:1$) is written as Au_3Pd_1 , $0.5 \text{ mmol} \cdot \text{L}^{-1} \text{HAuCl}_4$ and $0.5 \text{ mmol} \cdot \text{L}^{-1} \text{H}_2\text{PdCl}_4$ and $0.1 \text{ mol} \cdot \text{L}^{-1} \text{KCl}$ ($C_{\text{HAuCl}_4}:C_{\text{H}_2\text{PdCl}_4}=1:1$) as Au_1Pd_1 , and $0.25 \text{ mmol} \cdot \text{L}^{-1} \text{HAuCl}_4$ and $0.75 \text{ mmol} \cdot \text{L}^{-1} \text{H}_2\text{PdCl}_4$ and $0.1 \text{ mol} \cdot \text{L}^{-1} \text{KCl}$ ($C_{\text{HAuCl}_4}:C_{\text{H}_2\text{PdCl}_4}=1:3$) as Au_1Pd_3 . Furthermore, the simplified form Au_1 and Pd_1

denotes a solution of $1 \text{ mmol}\cdot\text{L}^{-1}$ HAuCl_4 and $0.1 \text{ mol}\cdot\text{L}^{-1}$ KCl and $1 \text{ mmol}\cdot\text{L}^{-1}$ H_2PdCl_4 and $0.1 \text{ mol}\cdot\text{L}^{-1}$ KCl , respectively. Agarose stamps were separately soaked in the respective solutions for 8 hours and then applied to fabricate AuPd alloy patterns with different compositions. As shown in Figure 1a, the electrolyte in the stamp could be directed and supplied preferentially to the small contact area between the workpiece and the agarose. Selective cathodic deposition could be achieved on the contact area owing to the constant supply of electrolyte from the agarose stamp to the interface. Thus, metal patterns with different AuPd compositions could be formed by selective electrochemical deposition on the contact area between the agarose and the ITO and the deposition of AuPd patterns onto ITO was controlled at a potential of -0.2 V for 1000 s , as shown in Figure 1b. Figure 1c shows a photograph of the apparatus for EWETS; a microscope was set up to image the transparent ITO during the process of microfabrication and to control the relative position between each fabrication cycle.

2.2. SEM, AFM, and XRD Characterization.

Surface topographies and bulk compositions of the AuPd NP arrays were assessed using a field-emission scanning electron microscope (FE-SEM, NOVA NANO SEM230) equipped with an X-ray detector for energy-dispersive X-ray analysis. The deposited bands on the ITO surface were characterized by tapping mode AFM (Nano IIIID, Bruker, USA). XRD measurements were applied to confirm the structural features of the AuPd co-deposits on the ITO, using a Philips powder diffraction system X'Pert Pro MPD (The Netherlands) with Cu-K_α radiation. The diffraction angle was scanned

over the range 34–90° with a 2 θ step size of 0.02°. The accelerating voltage was set at 40 kV.

2.3. Electrochemical Measurements.

Electrochemical measurements were conducted on a CHI842B electrochemistry workstation (Shanghai Chenhua instrument Corporation, China) using a three-electrode system, where ITO served as the working electrode. A Pt wire and an Ag/AgCl electrode served as the counter and reference electrode, respectively. Cyclic voltammograms of the bulk AuPd alloys on ITO in a solution of 10 mmol·L⁻¹ H₂O₂ and 0.1 mol·L⁻¹ Na₂SO₄ were acquired to investigate their electrocatalytic behavior for H₂O₂ reduction. The electrolyte was deoxygenated by bubbling nitrogen through it prior to each experiment, and a nitrogen blanket was kept flowing over the cell during the measurements. The bulk AuPd alloys on ITO were prepared by electrochemical deposition. The ITO with a geometric area of 1 × 1 cm² was soaked in the solutions with different AuPd compositions and then the deposition potential of -0.2 V was kept for 1000s to fabricate bulk AuPd alloys on ITO.

2.4. SECM Characterization.

Electrocatalytic properties were determined at room temperature using a CHI920C SECM instrument (Shanghai Chenhua instrument Corporation, China) with a four-electrode system. The substrate electrode bearing an AuPd alloy NP array on ITO was mounted in a SECM Teflon cell. An inverted microscope beneath the ITO substrate was used to observe the relative distance and position between the tip and the

transparent substrate in order to move the tip along the band accurately. An Ag/AgCl electrode and a platinum wire were employed as the reference and counter electrodes, respectively. A Pt ultramicroelectrode (UME; radius of 11.45 μm) with $\text{RG} = 3$ (for details of disk UME characterization, see Supporting Information Section S1) was adopted as the SECM tip. The tip–substrate distance was determined by the positive approach curves obtained with an aqueous solution containing 0.1 $\text{mmol}\cdot\text{L}^{-1}$ FcMeOH and 0.1 $\text{mol}\cdot\text{L}^{-1}$ KCl. During the positioning experiment, the tip potential was held at 0.5 V, while the potential of the AuPd array substrate was held at 0 V to ensure purely diffusion-controlled conditions.

Fig. 2 shows a schematic representation of the reactions taking place in the gap between the tip and the substrate when the SECM was working in the SG-TC and RC-SECM modes, respectively. In Fig. 2a, FcMeOH was oxidized to FcMeOH^+ (ferricenium methanol) at a tip potential of 0.5 V and the substrate potential was set at 0.1 V for reduction back to FcMeOH (ferrocenemethanol). In contrast, the tip potential and the substrate potential in RC-SECM were both biased at -0.2 V in an aqueous solution containing 10 $\text{mmol}\cdot\text{L}^{-1}$ H_2O_2 and 0.1 $\text{mol}\cdot\text{L}^{-1}$ Na_2SO_4 . In the RC-SECM mode, H_2O_2 could be simultaneously reduced at the tip and in the sample in competition. The reductive current of H_2O_2 at the tip will become smaller with higher electrocatalytic activity since more H_2O_2 will be consumed at the substrate.

3. Results and Discussion

3.1. Surface Morphology and Microstructure.

Catalysts with various compositions were fabricated by the electrochemical wet-stamping technique, and the deposition of AuPd patterns onto ITO was controlled at a potential of -0.2 V for 1000 s. The optical image in Fig. 3e shows lines from top to bottom made of Au and AuPd alloys that were fabricated from the patterned agarose stamp containing solutions of Au₁, Au₃Pd₁, Au₁Pd₁, and Au₁Pd₃; the width of the arrays was 50 μm . Magnified SEM images are shown in Fig. 3 (a)–(d). Fig. 3 (a) shows that the straight line deposited by the agarose stamp containing Au was made up of flower-like NPs with a diameter of 350 nm, whereas the NPs deposited from Au₃Pd₁ and Au₁Pd₁ were smaller with diameters of 300 nm and 250 nm, respectively. The remarkable change in the surface morphologies of the AuPd catalysts points to a complicated mechanism of the electrodeposition process. That is to say, with increasing Pd content, the nucleation process of the alloy NPs on ITO most likely changes from progressive nucleation to instantaneous nucleation. The concentration ratio between chloroauric acid and chloropalladic acid had a significant influence on the composition of the AuPd alloy. In our previous work[33, 34], it has been proved that a higher concentration of Au ions led to Au-rich alloy NPs, and a higher concentration of Pd ions led to Pd-rich alloy NPs. The surface morphologies of the AuPd co-deposits were further characterized by AFM, as shown in Fig. S2. The size distribution of NPs in the patterns characterized by AFM was similar to that discerned from the SEM images.

3.2. Characterization of the Bulk Structure Composition by XRD and EDS

Concerning the bulk composition of Pd and Au in the alloyed NPs, EDX proved to be a

useful tool. The EDX spectra showed atomic percentages (at. %) of Au in the NPs of 100, 68.95, 52.45, and 28.81, corresponding to Au₁, Au₃Pd₁, Au₁Pd₁, and Au₁Pd₃. XRD is also an invaluable method for investigating the solid structure of metal nanoparticles and the compositions of alloy particles. Fig. 4 (a) illustrates XRD patterns of the bulk electrodes deposited from the solutions of Au₁, Au₃Pd₁, Au₁Pd₁, Au₁Pd₃, and Pd₁ on ITO. Apart from the peaks labeled (*) attributable to ITO, each pattern exhibits three diffraction peaks in the range $35^\circ < 2\theta < 90^\circ$, which can be indexed to the electrodeposits. The diffractograms showed peaks at $2\theta = 44.7^\circ$, 51.9° , and 76.7° and at 47.0° , 54.7° , and 81.1° , attributable to the (111), (200), and (220) planes of Au and Pd with an fcc structure. In addition, the diffraction peaks of the co-deposits from the solutions of Au₃Pd₁, Au₁Pd₁, and Au₁Pd₃ exhibited an incremental peak shift from pure Au to pure Pd with increasing Pd content, which indicated alloy formation between Au and Pd rather than mere physical mixtures giving rise to overlapping lines of the two pure metals. The atomic composition could be calculated from the lattice parameter shifts by the angular position of the (111), (200), and (220) diffractions according to Vegard's law, as shown in Table 1. For Au₃Pd₁, Au₁Pd₁, and Au₁Pd₃, the atomic contents of Au were estimated to be 81.5%, 51.2%, and 21.1%, respectively. The values obtained by EDX and XRD are very similar, and any differences might stem from the different sample preparation methods. In the former case, it was deposited by an agarose stamp containing the electrolyte, whereas in the latter case it was prepared by bulk electrodeposition from the mixed solution.

3.3. Electrocatalytic Properties for Reduction of H₂O₂.

Since the catalytic activity towards electrochemical reduction could be adjusted by changing the compositions of the alloy NPs, it was of interest to investigate the influence of catalytic properties when the presence of the second noble metal(Pd) in the codeposits. Fig. 4 (b) shows the cyclic voltammograms of Au₁, Au₃Pd₁, Au₁Pd₁, and Au₁Pd₃-modified ITO electrodes in N₂-saturated 10 mmol·L⁻¹ H₂O₂ and 0.1 mol·L⁻¹ Na₂SO₄. The reduction peak potentials of Au₃Pd₁, Au₁Pd₁, Au₁Pd₃, and Pd₁ were -0.26, -0.27, -0.35, and -0.50 V, respectively. The less negative the reduction peak potential of the alloy, the more active the alloy metal for electrocatalysis. As shown in Table 1, the Au₃Pd₁ electrode showed the least negative reduction peak and the highest current density in the reduction reaction of H₂O₂; that is to say, the Au₃Pd₁ electrode showed better catalytic activity than Au₁Pd₁ or Au₁Pd₃. The order of catalytic ability was Au₃Pd₁ > Au₁Pd₁ > Au₁Pd₃ > Au₁. The calculation process for estimating the real surface area of the electrode is elaborated in Fig. S3.

The RC-SECM mode is based on the competition between the tip and the active areas of the substrate for the same redox species, and obvious differences in tip current were observed as the tip passed over the respective electrocatalysts. Fig. 5(a and b) shows the RC-SECM mode images of H₂O₂ reduction on a series of AuPd electrocatalyst arrays in 10 mmol·L⁻¹ H₂O₂ and 0.1 mol·L⁻¹ Na₂SO₄. The tip and the substrate were both biased at -0.2 V, at which H₂O₂ reduction can take place. The tip-substrate distance was controlled at about 15 μm. As can be seen in Fig. 5c, different tip currents were

observed in the probe scan curve, and the Au₃Pd₁ band showed the lowest current of about 0.92×10^{-8} A among all of the bands; that is to say, the Au₃Pd₁ band showed the highest activity for the H₂O₂ reduction. This conclusion is in accordance with the result of the cyclic voltammogram in H₂O₂ solution in Fig. 4 (b).

3.4. Determination of the Heterogeneous Electron-Transfer Rates at AuPd Arrays.

SECM approach curves, which are dependent on the substrate reaction rate, represent a very powerful tool for kinetic studies of heterogeneous reactions on AuPd array substrates. We have used SECM to characterize the charge-transfer processes occurring at the AuPd array electrodes during the reduction of ferricenium methanol, whereby the feedback current of the tip is dependent on the heterogeneous electron-transfer (HET) capability of the local area on the AuPd array. Positive feedback behavior during the approach of the UME to the AuPd array is indicative of enhanced electron transfer between them. Such electron transfer regenerates the FcMeOH mediator in the AuPd array, causing an enhancement of the current.

Fig. 6 (a) presents a SECM image of the AuPd arrays. It can clearly be observed that the feedback currents above the AuPd arrays are different from each other, and that the Au₃Pd₁ band presents the highest current among all the bands in the respective arrays. That is to say, the Au₃Pd₁ band showed the highest activity for FcMeOH reduction. From the SECM image, we can conclude that the electrochemical activities of the AuPd alloys with different compositions were Au₃Pd₁ > Au₁ > Au₁Pd₁ > Au₁Pd₃.

The kinetic rate constant can be extracted from the fitting of an experimental I_T - L curve

(the so-called approach curve, where I_T is the tip current and L is the distance between the tip and the substrate) to the theoretical curve. Fig. 6 (b) shows the normalized current of I_T - L curves for a Pt tip of diameter 11.45 μm when the UME approached the substrate. The value L is the ratio of the distance of the UME from the substrate to the radius of the UME. The UME was immersed in a 1 $\text{mmol}\cdot\text{L}^{-1}$ FcMeOH and 0.1 M KCl solution. The Pt tip potential was held at $E_T = 0.5$ V to ensure oxidation of FcMeOH under diffusion-limited conditions, and the substrate potential was held at $E_{\text{sub}} = 0.1$ V to reduce the FcMeOH⁺ species generated at the tip. As shown in Fig. 6 (b), the finite element modeling method was used to simulate the tip current response as a function of the standard HET rate constant (k_0) through COMSOL Multiphysics 4.3b (details are provided in Supporting Information Section S4), and the simulated probe approach curve with different values of k_0 could be readily fitted to the experimental current curves. We could thereby obtain the k_0 for each AuPd alloy: k_0 values of 0.02, 0.5, 0.01, and 0.006 cm/s were obtained for Au₁, Au₃Pd₁, Au₁Pd₁, and Au₁Pd₃, respectively. Because a higher value of k_0 indicates better electrochemical activity, the Au sample and AuPd alloys can be arranged in the order Au₃Pd₁ > Au₁ > Au₁Pd₁ > Au₁Pd₃. These results are in accordance with those from the SECM image.

4. Conclusion

AuPd electrocatalyst arrays with four different compositions have been successfully synthesized on an ITO surface by EWETS using electrolyte mixtures with different concentration ratios of H₂AuCl₄ and H₂PdCl₄. The proposed technique for the

preparation of electrocatalyst arrays is simple, fast, and does not require expensive equipment. The composition of the AuPd alloy nanoparticles can be controlled by adjusting the concentration of the electrolyte. The presence of Pd in the co-deposits greatly influences both the surface morphology and electrocatalytic activity. The electrochemical properties of the arrays have been investigated by electrochemical techniques and different operating modes of SECM. SECM screening of the AuPd electrocatalyst arrays suggested that the Au_3Pd_1 electrocatalyst showed superior activities among the respective alloys in H_2O_2 and FcMeOH^+ reduction reactions. The SECM results were further confirmed by cyclic voltammetry experiments and calculation of heterogeneous electron-transfer rates, which proved that the SECM was applicable for the screening of multicomponent alloy catalysts and determining the optimal composition for electrocatalytic reactions.

Acknowledgement

This study was financially supported by the National Science Foundation of China (21573043, 21173048).

References

- [1] D. A. Walsh, J. L. Fernández, A. J. Bard, Rapid Screening of Bimetallic Electrocatalysts for Oxygen Reduction in Acidic Media by Scanning Electrochemical Microscopy, *J. Electrochem. soc* 153 (2006) E99-E103.

- [2] R. Potyrailo, K. Rajan, K. Stoewe, I. Takeuchi, B. Chisholm, H. Lam, Combinatorial and High-Throughput Screening of Materials Libraries: Review of State of the Art, *ACS Comb Sci* 13 (2011) 579-633.
- [3] W. J. Bowyer, J. Xie, R.C. Engstrom, Fluorescence Imaging of the Heterogeneous Reduction of Oxygen, *Anal. Chem.* 68 (1996) 2005-2009.
- [4] X. Lin, L. Zheng, G. Gao, Y. Chi, G. Chen, Electrochemiluminescence Imaging-Based High-Throughput Screening Platform for Electrocatalysts Used in Fuel Cells, *Anal. Chem.* 84 (2012) 7700-7707.
- [5] E. Terreno, D.D. Castelli, A. Viale, S. Aime, Challenges for Molecular Magnetic Resonance Imaging, *Chem. Rev.* 110 (2010) 3019-3042.
- [6] A. J. Bard, F.R. F. Fan, D. T. Pierce, P. R. Unwin, D. O. Wipf, and F. Zhou, Chemical Imaging of Surfaces with the Scanning Electrochemical Microscope, *Science*, 254(1991) 68-74.
- [7] A. J. Bard, F. R. F. Fan, J. Kwak, and O. Lev, Scanning Electrochemical Microscopy. 1. Introduction and Principles, *Anal. Chem.* 61 (1989) 132-138.
- [8] A. J. Bard, F. R. F. Fan, D. T. Pierce, P. R. Unwin, D. O. Wipf, F. Zhou, Chemical Imaging of Surfaces with the Scanning Electrochemical Microscope, *Science* 254 (1991) 68-74.
- [9] J. H. Zhong, J. Zhang, X. Jin, J. Y. Liu, Q. Y. Li, M. H. Li, W. Cai, D. Y. Wu, D. P. Zhan, B. Ren, Quantitative Correlation between Defect Density and Heterogeneous Electron Transfer Rate of Single Layer Graphene, *J. Am. Chem. Soc.* 136 (2014)

16609-16617.

[10] Y. Shen, M. Trauble, G. Wittstock, Detection of Hydrogen Peroxide Produced during Electrochemical Oxygen Reduction Using Scanning Electrochemical Microscopy, *Anal. Chem.* 80 (2008) 750-759.

[11] C. M. Sánchez-Sánchez, A.J. Bard, Hydrogen Peroxide Production in the Oxygen Reduction Reaction at Different Electrocatalysts as Quantified by Scanning Electrochemical Microscopy, *Anal. Chem.* 81 (2009) 8094-8100.

[12] M. A. Mezour, R. Cornut, E.M. Hussien, M. Morin, J. Mauzeroll, Detection of Hydrogen Peroxide Produced during the Oxygen Reduction Reaction at Self-Assembled Thiol-Porphyrin Monolayers on Gold using SECM and Nanoelectrodes, *Langmuir* 26 (2010) 13000-13006.

[13] X. M. Shen, W. Q. Liu, X. J. Gao, Z. H. Lu, X. C. Wu, X. F. Gao, Mechanisms of Oxidase and Superoxide Dismutation-like Activities of Gold, Silver, Platinum, and Palladium, and Their Alloys: A General Way to the Activation of Molecular Oxygen, *J. Am. Chem. Soc.* 137 (2015) 15882–1589.

[14] A. Kafi, G. Wu, A. Chen, A novel hydrogen peroxide biosensor based on the immobilization of horseradish peroxidase onto Au-modified titanium dioxide nanotube arrays, *Biosens. Bioelectron.* 24 (2008) 566-571.

[15] W. Chen, S. Cai, Q. Q. Ren, W. Wen, Y. D. Zhao, Recent advances in electrochemical sensing for hydrogen peroxide: a review, *Analyst* 137 (2012) 49-58.

[16] K. Zhou, Y. Zhu, X. Yang, J. Luo, C. Li, S. Luan, A novel hydrogen peroxide

biosensor based on Au–graphene–HRP–chitosan biocomposites, *Electrochim. Acta* 55 (2010) 3055-3060.

[17] R. Burkitt, T. R. Whiffen, E. H. Yu, Iron phthalocyanine and MnO_x composite catalysts for microbial fuel cell applications, *Appl. Catal. B: Environ.* 181 (2016) 279-288.

[18] T. C. Nagaiah, D. Schäfer, W. Schuhmann, N. Dimcheva, Electrochemically Deposited Pd–Pt and Pd–Au Codeposits on Graphite Electrodes for Electrocatalytic H_2O_2 Reduction, *Anal. Chem.* 85 (2013) 7897-7903.

[19] T. C. Nagaiah, A. Maljusch, X. Chen, M. Bron, W. Schuhmann, Visualization of the Local Catalytic Activity of Electrodeposited Pt–Ag Catalysts for Oxygen Reduction by means of SECM, *ChemPhysChem* 10 (2009) 2711-2718.

[20] K. Eckhard, X. Chen, F. Turcu, W. Schuhmann, Redox competition mode of scanning electrochemical microscopy (RC-SECM) for visualisation of local catalytic activity, *PCCP* 8 (2006) 5359-5365.

[21] K. Eckhard, W. Schuhmann, Localised visualisation of O_2 consumption and H_2O_2 formation by means of SECM for the characterisation of fuel cell catalyst activity, *Electrochim. Acta* 53 (2007) 1164-1169.

[22] S. Schwamborn, L. Stoica, X. Chen, W. Xia, S. Kundu, M. Muhler, W. Schuhmann, Patterned CNT Arrays for the Evaluation of Oxygen Reduction Activity by SECM, *ChemPhysChem* 11 (2010) 74-78.

[23] J. L. Fernández, D. A. Walsh, A. J. Bard, Thermodynamic Guidelines for the

Design of Bimetallic Catalysts for Oxygen Electroreduction and Rapid Screening by Scanning Electrochemical Microscopy. M–Co (M: Pd, Ag, Au), *J. Am. Chem. Soc.* 127 (2004) 357-365.

[24] C. Jung, C. M. Sánchez-Sánchez, C.-L. Lin, J. n. Rodríguez-López, A. J. Bard, Electrocatalytic Activity of Pd–Co Bimetallic Mixtures for Formic Acid Oxidation Studied by Scanning Electrochemical Microscopy, *Anal. Chem.* 81 (2009) 7003-7008.

[25] C.-L. Lin, J. n. Rodríguez-López, A. J. Bard, Micropipet Delivery–Substrate Collection Mode of Scanning Electrochemical Microscopy for the Imaging of Electrochemical Reactions and the Screening of Methanol Oxidation Electrocatalysts, *Anal. Chem.* 81 (2009) 8868-8877.

[26] J. L. Fernández, A. J. Bard, Scanning Electrochemical Microscopy. 47. Imaging Electrocatalytic Activity for Oxygen Reduction in an Acidic Medium by the Tip Generation–Substrate Collection Mode, *Anal. Chem.* 75 (2003) 2967-2974.

[27] J. L. Fernández, J. M. White, Y. Sun, W. Tang, G. Henkelman, A. J. Bard, Characterization and Theory of Electrocatalysts Based on Scanning Electrochemical Microscopy Screening Methods†, *Langmuir* 22 (2006) 10426-10431.

[28] A. W. Hassel, K. Fushimi, M. Seo, An agar-based silver|silver chloride reference electrode for use in micro-electrochemistry, *Electrochem. Commun.* 1 (1999) 180-183.

[29] L. Zhang, J. L. Zhuang, X. Z. Ma, J. Tang, Z. W. Tian, Microstructuring of p-Si(100) by localized electrochemical polishing using patterned agarose as a stamp, *Electrochem. Commun.* 9 (2007) 2529-2533.

- [30] J. Tang, J. L. Zhuang, L. Zhang, W. H. Wang, Z. W. Tian, Cu micropatterning on n-Si(111) by selective electrochemical deposition using an agarose stamp, *Electrochim. Acta* 53 (2008) 5628-5631.
- [31] J. Tang, L. Zhang, X. Tian, Micromachining on copper and nickel by electrochemical wet stamping, *J. Micromech. Microeng.* 20 (2010) 115030.
- [32] I. T. Bensemann, M. Fialkowski, B. A. Grzybowski, Wet Stamping of Microscale Periodic Precipitation Patterns. *J. Phys. Chem. B* 109 (2004) 2774-2778.
- [33] J. Tang, X. C. Tian, W. H. Pang, Y. Q. Liu, J. H. Lin, Codeposition of AuPd bimetallic nanoparticles on to ITO and their electrocatalytic properties for ethanol oxidation. *Electrochim. Acta* 81 (2012) 8-13.
- [34] T. Y. Su, X. J. Xiao, M. W. Ye, X. C. Tian, J. H. Lin, J. Tang, Preparation of AuPd and Au Microarrays on ITO and Characterization of Electrocatalytic Activity with SECM. *Acta Phys. -Chim. Sin.* 30 (2014) 325-330.

Figure captions

Figure 1 Illustration of the procedure for fabricating AuPd alloy NP arrays by EWETS using a micropatterned agarose stamp with different solutions (a). Schematic diagram of electrochemical wet-stamping technique (b) and apparatus of device (c).

Figure 2 Schematic representation of the reactions taking place in the gap between the tip and substrate in (a) SG-TC mode and (b) RC-SECM mode.

Figure 3 SEM images of (a) Au₁ and (b)–(d) AuPd arrays with different concentration ratios in the electrolyte: (a) Au₁, (b) Au₃Pd₁, (c) Au₁Pd₁, and (d) Au₁Pd₃; insets show the EDX spectra; (e) optical micrograph of the AuPd arrays.

Figure 4 (a) XRD analysis of AuPd electrodeposits with different concentration ratios in the electrolytes. (b) Cyclic voltammograms of AuPd electrodeposits on ITO in 10 mmol·L⁻¹ H₂O₂ and 0.1 mol·L⁻¹ Na₂SO₄. Scan rate: 50 mV·s⁻¹.

Figure 5 (a and b) The 2D and 3D SECM RC-mode images of AuPd band arrays and (c) corresponding probe scan curve in 10 mmol·L⁻¹ H₂O₂ and 0.1 mol·L⁻¹ Na₂SO₄. Scan rate = 25 μm/s. Dashed line indicate the scanning direction is from position 1 to position 2.

Figure 6 (a) SECM image of the AuPd band arrays in 0.1 mmol·L⁻¹ FcMeOH and 0.1 mol·L⁻¹ KCl. (b) Comparison of the experimental (solid lines) and theoretical (symbols) SECM approach curves on AuPd arrays with different compositions in 1 mmol·L⁻¹ FcMeOH and 0.1 mol·L⁻¹ KCl. E_{tip} = 0.5 V, E_{sub} = 0.1 V vs. Ag/AgCl.

Table 1 Atomic contents of Au in the AuPd alloys calculated from the XRD spectra compared with those measured from EDS spectra, the real surface areas of the AuPd

alloys, and the potential and peak current densities of the AuPd alloys in the H_2O_2 reduction reaction.

Table(s)

Deposition solution	2θ ($^{\circ}$)	$d(111)$ ($\text{\AA}$)	C_{Au} (XRD,%)	C_{Au} (EDS,%)	Reduction peak potential (V)	Surface area (cm^2)	Peak current density ($\times 10^{-3}$ $\text{A}\cdot\text{cm}^{-2}$)
Au ₁	44.700	2.3523	100	100	/	1.774	/
Au ₃ Pd ₁	45.120	2.3316	81.5	68.95	-0.26	2.284	-0.813
Au ₁ Pd ₁	45.820	2.2978	51.2	52.45	-0.27	2.326	-0.805
Au ₁ Pd ₃	46.540	2.2642	21.1	28.81	-0.35	3.074	-0.568
Pd ₁	47.059	2.2406	0	0	-0.50	3.212	-0.565

* $C_{\text{Au}}(\text{XRD})$ are the atomic contents of Au estimated by XRD; $C_{\text{Au}}(\text{EDS})$ are the atomic contents of Au measured by EDS.

Figure %

Figure 8

Figure Y'

Figure(

Figure)

(a)

(b)

(c)

Figure*