Copper-enriched Palladium-Copper alloy nanoparticles for effective electrochemical formic acid oxidation

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Abstract: In this work, Pd-Cu alloy nanoparticles (NPs) with different atomic ratios are prepared on functionalized carbon nanotubes (CNTs) and applied as electrocatalysts for formic acid oxidation. The Cu-enriched Pd-Cu alloy NPs exhibit improved electrocatalytic activity and stability. Functionalized carbon supports are applied as substrates to tune the nanoscale morphologies of the obtained bimetallic phases under appropriate calcination and hydrogenation treatments. Spill-over effect aids a reduction of a high weight loading of Cu in its metallic phase, in turn, these Cu atoms integrate into Pd lattice and isolate Pd neighboring atoms. Surface analyses show that a certain amount of the isolated Pd remains on the surfaces of Pd-Cu alloy NPs, which is responsible for the enhanced electrocatalytic performance.

Keywords: formic acid, Copper-enriched, Palladium-Copper alloy, carbon nanotube

1. Introduction

In recent years, formic acid, which represents a new feedstock for fuel cells, has been widely investigated because it is non-toxic and exhibits a low crossover rate through Nafion membranes. Direct formic acid fuel cells (DFAFCs) have favourable oxidation kinetics, low operating temperatures, and high theoretical open-circuit potentials, and they effectively overcome the H_2-storage and transport problems associated with proton-exchange membrane fuel cells (PEMFCs) and the toxicity of the methanol used in direct methanol fuel cells (DMFCs). Thus, they open up a pathway for the development of a new type of portable power[1-3].

Currently, the catalytic materials that are most commonly used as fuel cell anodes are Pt-based alloys[4,5]. However, Pt resources are limited, expensive, and prone to carbon monoxide (CO) poisoning, and thus, the application of Pt catalysts is limited[3,6,7]. Pd and Pt are elements of the same group and have similar characteristics, including face-centred cubic (fcc) crystal structures and similar atomic sizes. Pd-based catalysts are considered to be better electrocatalysts than Pt-based ones because the reaction on the Pd surface follows a direct pathway. Nevertheless, the inferior electrocatalytic stability of Pd catalysts has limited their development[8]. Introducing structural modifications by adding foreign atoms to generate Pd-based alloys has been investigated to enhance the catalytic activity at low overpotentials and increase the stability of Pd-based catalysts. However, the practical application of Pd-based alloys as electrocatalysts for DFAFCs remains challenging. First, Pd and other added metals have been reported to exceed 20-30 wt%[9, 10]. Using this amount of metals prohibits the metal dispersion in nanoscale and limits the accessible

surface areas during catalysis. Second, the effects of the surface electronic properties and structural stabilities of bimetallic compounds (controlled by bonding patterns) on HCOOH oxidation remain unclear.

Herein, Pd-Cu alloys with various Pd:Cu molar ratios are fabricated on carbon nanotubes (Pd_xCu_y/CNTs) for catalytic studies in HCOOH oxidation. Functionalized CNTs embed nanocrystals of the formed alloy particles and facilitate their nanoscale dispersion during calcination and reduction treatments. The HCOOH oxidation results indicate that Cu-enriched Pd-Cu alloy NPs exhibit enhanced activity and stability relative to the other Pd_xCu_y alloys with lower Cu contents. Furthermore, surface and structural analyses reveal that the surface electronic properties of Cu-enriched Pd-Cu alloy NPs may govern the catalytic pathways.

2. Materials and methods

PR24 low-heat-treated (LHT) CNTs (1g) were functionalized by oxidation in concentrated HNO_3 (300mL) for 1 h at 120°C[11]. Pd_xCu_y/CNTs (where x:y = 1:0, 3:1, 1:1, 1:3, or 0:1) were synthesized as following: in the case of Pd_1Cu_3/CNTs, 31.8 μL of $Pd(NO_3)_2$ (10 wt%, Sigma–Aldrich) solution, 11.2 mg $Cu(NO_3)_2$ (Sigma-Aldrich) were mixed into 20ml ethanol, followed by adding 50 mg of CNTs to allow coordination with functionalities as anchoring sites. Stirring was maintained at 45℃ throughout the impregnation process until the solution had dried. The collected powder was calcined in a muffle for 2h at 250°C and then annealed in a tube furnace for 2h at 250°C under a He/H_2 atmosphere (He, 100 mL/min; H_2, 25 mL/min). The preperation of other samples were same to this method. The atom ratios in terms

X-ray diffraction (XRD) was performed using a Bruker D8 Advance XRD instrument with Cu-Kα radiation. An aberration-corrected JEOL JEM-ARM200CF transmission electron microscope was employed to investigate structural and chemical properties in STEM mode. X-ray photoelectron spectroscopy (XPS) was conducted with a Thermo ESCALAB 250 XPS instrument using a monochromatic Al Kα source (1486.6 eV).

3. Results and Discussion

Fig. 1a shows the dispersion of Pd-Cu NPs on the Pd_1Cu_3/CNT. Fig. 1b presents the high-resolution scanning TEM (HR-STEM) image of a Pd-Cu alloy NP on the Pd_1Cu_3/CNTs. The HR-STEM image shows that the interplanar distances were 0.220 nm and presents two sets of (111) planes with an acute angle 70.5°. Fig. 1c is the STEM image of dispersed Pd-Cu alloy NP on the Pd_1Cu_3/CNT, and Figs. 1（d-e）present the STEM-energy-dispersive X-ray spectroscopy (EDX) element mapping distributions of Pd and Cu, respectively. Based on the STEM-EDX elemental mapping, Cu and Pd are homogeneously distributed within the NPs. Fig. 1 indicates the alloying states of the nanocatalysts. The lattice parameters of fcc Pd and Cu metals are 0.226 and 0.208 nm, respectively, and the lattice parameters of the alloying NPs fall between these values.

Fig. 2 shows the XRD patterns of the Pd/CNTs, Pd_xCu_y/CNTs, and Cu/CNTs samples. The Pd/CNTs sample shows peaks at 40.1° (Pd(111)), 46.7° (Pd(200)), and 68.1° (Pd(220)), suggesting the synthesis of Pd NPs (JCPDS standard Pd 46-1043). The Cu/CNTs sample shows peaks at 43.3° (Cu(111)) and 50.4° (Cu(200)), indicating the synthesis of Cu NPs (JCPDS standard 04-0836(Cu)). The peaks located at ~42.8° for the Pd_1Cu_1/CNTs, Pd_3Cu_1/CNTs, and Pd/CNTs samples correspond to the C(101) reflection planes of carbon (JCPDS standard C 26-1077). Fig. 2(b–d) show that the Pd peaks broaden and the 2θ angles increase from 40.1 to 41.4° as the Cu content increases, indicating that the Cu atoms have entered the Pd crystal to generate a fcc Pd-Cu alloy structure[12, 13]. It should be noted that systems containing two or more metallic species may exist in several phases. The Pd_1Cu_3/CNTs show a perturbation peak at 41.3°, indicating that a PdCu intermetallic phase (JCPDS standard 48-1551 (CuPd)) may have formed within the Pd_1Cu_3/CNTs sample.

XPS was further utilized to examine the surface compositions and valence electronic structures of Pd_xCu_y/CNTs catalysts. Upon addition of Cu, the original Pd peak profile is gradually weakened (Fig. 3A). However, the preserved Pd 3d spectra on all the Pd_xCu_y/CNTs indicates that some Pd in monometallic phase remains dispersed on the catalyst surfaces. On the other hand, Fig. 3B shows a higher Cu^0 peak on the Pd_1Cu_3/CNTs than on the Cu/CNTs. Owning to the fact that more Cu (5.3wt.%) is present in Pd_1Cu_3/CNTs than in Cu/CNTs (3wt.%), we propose that the enhanced Cu^0 peak on Pd_1Cu_3/CNTs was caused by the spillover effect. In this process, the H_2 adsorbed on the noble metal surfaces decomposes to H atoms, and

these dissociative H atoms migrate to alloyed metals or supporting oxides[14,15]. Accordingly, spill-over effects is known to exert significant influences in the field of heterogeneous catalysis by shaping and affecting the supported active phases[16].

The catalytic activities of these Pd_xCu_y/CNTs catalysts were investigated by cyclic voltammetry (CV). Fig. 4A shows the mass activities of Pd_xCu_y/CNTs catalysts for formic acid electrooxidation. The potentials of both Pd_1Cu_3/CNTs and Pd/CNTs are 0.15 V, whereas those of both Pd_3Cu_1/CNTs and Pd_1Cu_1/CNTs are 0.14 V.

No obvious difference was noticed in the anodic peak potential. For comparison, the mass activity of Pd_1Cu_3/CNTs is 560 A g^{-1}, whereas that of Pd/CNTs is 487 A g^{-1}. Thus, the Pd_1Cu_3/CNTs catalyst is more active than the Pd/CNTs catalyst for formic acid oxidation. The mass activity of Pd_3Cu_1/CNTs is 238 A g^{-1}, and that of Pd_1Cu_1/CNTs is 270 A g^{-1}. The activities of these two samples were lower than that of Pd/CNTs. To further confirm the activities of the Pd_1Cu_3/CNTs and Pd/CNTs catalysts, chronoamperometry tests were conducted in 0.5-M H_2SO_4 and 0.5-M HCOOH at 0.15 V for 3600 s. As shown in Fig.4B, during the first 1000 s, the mass activities of Pd_1Cu_3/CNTs, Pd/CNTs, Pd_3Cu_1/CNTs, and Pd_1Cu_1/CNTs were 17.7 A g^{-1}, 11.0 A g^{-1}, 6.9 A g^{-1}, and 2.1 A g^{-1}, respectively. After 1000 s, the mass activities of the four samples stabilized, and that of Pd_1Cu_3/CNTs remained higher than those of the others.

The electrochemical activity surface area (EASA) is one of the important standards for catalysts. Typically, CO-stripping measurements are used to estimate the

EASA of Pd-based catalysts. The specific EASA was calculated according to the following equation:

$$EASA=Q/(mC) \qquad (1)$$

where Q is the charge for CO-desorption electrooxidation, m is the Pd loading amount, and C is the charge needed for the adsorption of a CO monolayer ($C=420$ μC cm^{-2}).

The EASA values are 38.4 m^2 g^{-1} for Pd/CNTs, 32.5 m^2 g^{-1} for Pd$_1$Cu$_3$/CNTs, 31.7 m^2 g^{-1} for Pd$_1$Cu$_1$/CNTs, and 29.8 m^2 g^{-1} for Pd$_3$Cu$_1$/CNTs. The specific area values were calculated in terms of the ratio of the mass activity and EASA. The specific activities of Pd/CNTs, Pd$_1$Cu$_3$/CNTs, Pd$_1$Cu$_1$/CNTs, and Pd$_3$Cu$_1$/CNTs are 12.7 A m^2, 17.2 A m^2, 8.5 A m^2, and 8.0 A m^2, respectively. These values confirm the enhanced electrocatalytic activity of Pd$_1$Cu$_3$/CNTs.

Previous reports have addressed the preparation of Pd-Cu bimetallic catalysts. Cu has been used to modify the Pd crystalline structure and surface electronic properties by forming alloy phases [12,17]. For example, Park[17] reported the generation of Pd-Cu/C catalysts with high electrocatalytic activity via chemical dealloying, which resulted in a porous dealloyed structure. Lu and co-workers[12] described a preparation method similar to that presented here, involving impregnation-reduction with NaBH$_4$ as a reductant. They found that a Pd-Cu/C catalyst with an atomic ratio of 3:1 exhibited the best electrocatalytic performance. In contrast, in this work, the Pd$_1$Cu$_3$/CNTs catalyst exhibited high electrocatalytic

activity for formic acid oxidation, which can be attributed to the geometrical isolation of Pd neighbouring atoms by introducing foreign metals in formed alloy NPs.

To modify the strengths of adsorption and desorption on Pd surfaces, Pd can be modified through the formation of intermetallics or alloys. In comparison to the dispersion difficulty of intermetallics caused by high temperature annealing treatments, the low-temperature synthesis of alloys facilitates obtaining nanoscale dispersions on supporting materials. In the current work, the surface functionalities identified on CNTs gave rise to an anchoring effect toward salt precursors. After the metal ions were coordinated with functional groups, hydrolysis was applied to crystallize the precursors nucleated on the oxidized carbon supports and generate nanocrystals[18,19]. During the synthesis, the aggregation of reduced Pd precursors via Ostwald ripening was hindered by interactions between Pd species and the CNTs surface functionalities[20]. The obtained Pd NPs were applied as anchoring sites for alloying reduced Cu via spill-over effect. The increased Cu peak in the XPS spectra in comparison to the other catalysts indicates that reduced Pd in its metallic phase caused the spill-over effect and directed the adsorbed H_2 to completely reduce the enriched amount of Cu. After integrating with Pd, the enriched Cu isolates Pd neighbouring atoms on Pa-Cu alloy NPs. In this work, because of the strong driving force for the dissolution of Cu in Pd, Pd-Cu bimetallic phases may have formed in the Pd_1Cu_3 NPs after calcination and hydrogenation treatments. Meanwhile, Pd is segregated by Cu and remained in the metallic phase in the Pd-Cu alloy NPs. Accordingly, the adsorption strength of the COOH intermediate is relatively weak on

nanosized Pd surfaces, thereby increasing the rate of formic acid oxidation to CO_2 (and the associated oxidation current).

4. Conclusions

In this work, we prepared Pd_xCu_y/CNTs catalysts with different atomic ratios through a simple impregnation method. The Pd_xCu_y/CNTs catalysts with different Pd:Cu atomic ratios exhibited markedly effect different for formic acid electrooxidation performances. During the deliberate thermal annealing treatments, carbon supports with surface functionalities were applied as substrates to crystallize the ion precursors and tune the nanoscale morphologies of the obtained Pd-Cu alloy NPs. The enhanced electrocatalytic activity and stability of Pd_1Cu_3/CNTs catalyst can be attributed to the geometrical isolation of Pd neighbouring atoms by introducing foreign metals in formed alloy NPs.

Acknowledgements

References

[1]. N. V. Rees, R. G. Compton, Sustainable energy: a review of formic acid electrochemical fuel cells. *Journal of Solid State Electrochemistry* 15(2011) 2095-2100.

[2]. O. Winjobi, Z. Zhang, C. Liang, W. Li, Carbon nanotube supported platinum–palladium nanoparticles for formic acid oxidation. *Electrochimica Acta* 55(2010) 4217-4221.

[3]. Y. Zhou, J. Liu, J. Ye, Z. Zou, J. Ye, J. Gu, T. Yu, A. Yang, Poisoning and regeneration of Pd catalyst in direct formic acid fuel cell. *Electrochimica Acta* 55(2010) 5024-5027.

[4]. M.M. Tusi, N.S.O. Polanco, S.G. Silva, E.V. Spinacé, A.O. Neto, The high activity of PtBi/C electrocatalysts for ethanol electro-oxidation in alkaline medium. *Electrochemistry Communications* 13(2011)143-146.

[5]. R.T. Lv, T.X. Cui, M.S. Jun, Q. Zhang, A.Y. Cao, D.S. Su, Z.J.Zhang, S.H. Yoon, J. Miyawaki, I. Mochida,F.Y. Kang, Open-ended, N-doped carbon nanotube-graphene hybrid nanostructures as high-performance catalyst support. *Advanced Functional Materials* 21(2011)999-1006.

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

[7]. V. Mazumder, S. Sun, Oleylamine-mediated synthesis of Pd nanoparticles for catalytic formic acid oxidation. *Journal of the American Chemical Society* 131(2009) 4588-4589.

[8]. R. Wang, S. Liao, S. Ji, High performance Pd-based catalysts for oxidation of formic acid. *Journal of Power Sources* 180(2008) 205-208.

[9]. G.J. Zhang, Y. Wang, X. Wang, Y. Chen, Y.M. Zhou, Y.W. Tang, L. Lu, J.C. Bao, T.H. Lu, Preparation of Pd–Au/C catalysts with different alloying degree and their electrocatalytic performance for formic acid oxidation. *Applied Catalysis B: Environmental* 102(2011) 614-619.

[10]. X. Wang, Y. Tang, Y. Gao, T. Lu, Carbon-supported Pd–Ir catalyst as anodic catalyst in direct formic acid fuel cell. *Journal of Power Sources* 175(2008) 784-788.

[11]. R. Villa, D. Wang, P. Spontoni, R. Arrigo, D.S. Su, L. Prati, Nitrogen functionalized carbon nanostructures supported Pd and Au–Pd NPs as catalyst for alcohols oxidation. *Catalysis Today* 157(2010) 89-93.

[12]. L. Lu, L. Shen, Y. Shi, T. Chen, G. Jiang, C. Ge, Y. Tang, Y. Chen, T. Lu, New insights into enhanced electrocatalytic performance of carbon supported Pd–Cu catalyst for formic acid oxidation. *Electrochimica Acta* 85(2012) 187-194.

[13]. K. Mandal, D. Bhattacharjee, P. S. Roy, S. K. Bhattacharya, S. Dasgupta, Room temperature synthesis of Pd–Cu nanoalloy catalyst with enhanced electrocatalytic activity for the methanol oxidation reaction. *Applied Catalysis A: General* 492(2015) 100-106.

[14]. W. Gao, N. Guan, J. Chen, X. Guan, R. Jin, H. Zeng, Z. Liu, F. Zhang, Titania supported Pd-Cu bimetallic catalyst for the reduction of nitrate in drinking water. *Applied Catalysis B: Environmental* 46(2003) 341-351.

[15]. R. Prins, Hydrogen spillover. Facts and fiction. *Chemical reviews* 112(2012) 2714-38.

[16]. W. C. Conner, J. L. Falconer, Spillover in heterogeneous catalysis. *Chemical reviews* 95(1995) 759-788.

[17]. K.H. Park, Y. W. Lee, S.W. Kang, S.W. Han, A facile one-pot synthesis and enhanced formic acid oxidation of monodisperse Pd–Cu nanocatalysts, *Chemistry – An Asian Journal* 6(2011) 1515 - 1519.

[18] C. Batchelor-McAuley, L.D. Shao, G.G. Wildgoose, M.L.H. Green, R.G. Compton, An electrochemical comparison of manganese dioxide microparticles versus [small alpha] and [small beta] manganese dioxide nanorods: mechanistic and electrocatalytic behaviour, *New Journal of Chemistry* 32 (2008) 1195-1203.

[19] X. Huang, L.D. Shao, G.W. She, M. Wang, S. Chen, X.M. Meng, Catalyst-free synthesis of single crystalline ZnO nanonails with ultra-thin caps, *CrystEngComm* 14 (2012) 8330-8334.

[20] L.D. Shao, X. Huang, D. Teschner, W. Zhang, Gold supported on graphene oxide: An active and selective catalyst for phenylacetylene hydrogenations at low temperatures, *ACS Catalysis* 4 (2014) 2369-2373.

Figure captions

Figure 1. (a) STEM image of Pd_1Cu_3/CNT. (b) HRTEM image of a Pd-Cu alloy NP on the Pd_1Cu_3/CNT. (c) STEM image of a dispersed Pd-Cu alloy NPs on the Pd_1Cu_3/CNT. (d) and (e) STEM-EDX element mapping distributions of Pd and Cu, respectively.

Figure 2. XRD patterns of the synthesized (a) Cu, (b) Pd_1Cu_3, (c)Pd_1Cu_1, (d)Pd_3Cu_1, and (e) Pd NPs. The black and red line represents Cu and PdCu standard in JCPDS, respectively.

Figure 3. XPS spectra of (A) Pd3d: (a) Pd_1Cu_3, (b) Pd_1Cu_1, (c) Pd_3Cu_1, and (d) Pd; and (B) Cu2p: (a) Cu, (b) Pd_1Cu_3, (c) Pd_1Cu_1, and (d) Pd_3Cu_1.

Figure 4. (A) CVs of catalysts in 0.5-M H_2SO_4 and 0.5-M HCOOH at a scan rate of 50 mVs^{-1}. (B) Chronoamperometry curves of catalyst samples in 0.5-M H_2SO_4 and 0.5-M HCOOH. (a) Pd_1Cu_3/CNTs, (b) Pd/CNTs, (c) Pd_3Cu_1/CNTs, and (d)

Pd$_1$Cu$_1$/CNTs.