

Short communication

Nanocrystalline tungsten carbide supported Au–Pd electrocatalyst for oxygen reduction

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Abstract

Au–Pd nanobimetallic particles supported on nanocrystalline tungsten carbide as electrocatalysts for oxygen reduction were prepared by an intermittent microwave heating (IMH) method. XRD measurement revealed that AuPd alloy formed during the IMH process. We showed these novel electrocatalysts could offer the activities that surpass that of the state-of-the-art Pt-based electrocatalysts for oxygen reduction reaction. The AuPd–WC/C electrode showed an over 70 mV shift towards more positive potentials compared to Pt/C electrode for ORR. The advantage seemed to come from the novel support of tungsten carbide which itself has the catalytic activity to enhance the catalytic activity of the metal electrocatalysts.

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1. Introduction

The design of catalytically active, stable and inexpensive electrocatalysts for the oxygen reduction reaction (ORR) is an urgent need for the fuel cells since the cost of the current proton exchange membrane fuel cells (PEMFCs) and direct alcohol fuel cells (DAFCs) is still prohibitive for broad commercialization. Recent efforts in electrocatalysis for ORR have been focused on the low Pt content or Pt alternative electrocatalysts [1–12]. We report a new Pt-free electrocatalyst that shows better performance than that currently used Pt-based electrocatalysts for ORR. It consists of Au–Pd nanobimetallic particles supported on tungsten carbide (denotes as AuPd–WC/C). The selection of tungsten carbide as support was based on the discovery of Levy and Boudart that tungsten carbide shows Pt-like behavior in surface catalysis [13]. The Au–Pd nanobimetallic particles prepared by different methods have been studied for the ORR [14,15]. Our previous work on Pt-free electrocatalysts demonstrated that

Ag nanoparticles supported on tungsten carbide (Ag–WC/C) show essentially equal performance compared to Pt/C electrocatalyst [4]. The development of more active and less expensive electrocatalysts will accelerate the application of fuel cells.

Recently, a new concept fuel cell using anion exchange membrane and selective electrocatalysts has been proposed [16–18]. It is conceivable that based on the research and development of both anode and cathode selective electrocatalysts and an anion exchange membrane as solid electrolyte, a mixed-reactant fuel cell would be assembled [19]. The authors' previous work on this new concept fuel cell focused on the development of the electrocatalysts used in alkaline media. In this study, five electrocatalysts, Au/C, Pt/C, Pd/C, Pd–WC/C and AuPd–WC/C, were tested for ORR in 1.0 M KOH solution at 25 °C.

AuPd–WC/C electrocatalyst with a mass ratio of Au:Pd:WC/C = 1:1:1 was prepared by intermittent microwave heating (IMH) method as reported previously [4,20]. The mixture of 2 mg as-prepared WC/C powder, 0.21 ml HAuCl₄ solution (4.78 mgAu ml⁻¹), 0.17 ml PdCl₂ solution (5.9 mgPd ml⁻¹) and excessive 1 M NaBH₄ solution was reacted for half an hour. The product was rinsed thoroughly using distilled–deionized water and centrifuged to remove

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sodium ions and neutralize the electrocatalyst. Typically, 1 mg electrocatalyst is mixed with 1.5 ml 2-propanol and ultrasonically treated for 20 min, resulting in uniformly dispersed AuPd–WC/C ink. A quantity of ink was then dropped onto the top surface of the graphite rod ($\Phi = 6$ mm) to make electrode. Finally, a drop of 0.5 wt% Nafion suspension (DoPont, USA) was covered on the top to prevent the damage of the electrocatalyst layer. For comparison, Au/C, Pt/C, Pd/C and Pd–WC/C were also prepared.

2. Experimental

All chemicals were of analytical grade and were used as received from the suppliers.

Preparation of electrocatalysts and electrodes: (1) tungsten carbide nanocrystals. Tungsten powder (1 g) was added into a mixture of 10 ml 30% (v/v) H_2O_2 , 5 ml 2-propanol and 10 ml water. The solution was left for 24 h before 1 g of Vulcan XC-72 carbon powder (Cabot Corp., USA) was added. The mixture was treated in an ultrasonic bath to form uniformly dispersed ink. The ink was dried in an oven and was then heated in a microwave oven with a heating procedure of 5 s on and 5 s pause for six times. The dried powder was used as the precursor of tungsten carbides. The precursor powder in the crucible was bubbling argon for 10 min and was further heated for 10 min by the intermittent microwave heating procedure. (2) Au and Pd supported on tungsten carbide electrocatalysts. Two milligrams as-prepared WC/C powder, 0.21 ml HAuCl_4 solution ($4.78 \text{ mg Au ml}^{-1}$), 0.17 ml PdCl_2 solution ($5.9 \text{ mg Pd ml}^{-1}$) and excessive 1 M NaBH_4 solution was reacted for half an hour. The product was rinsed thoroughly using distilled–deionized water and centrifuged to remove sodium ions and neutralize the electrocatalyst. Typically, 1 mg electrocatalyst is mixed with 1.5 ml 2-propanol and ultrasonically treated for 20 min, resulting in a uniformly dispersed AuPd–WC/C ink. (3) Electrodes. The graphite rod with diameter of 6 mm was used as electrode substrate and the top surface of the rod was pre-cleaned with sand paper. The uniformly dispersed AuPd–WC/C ink was then dropped onto the top surface of the graphite rod to prepare electrodes with different electrocatalyst loadings. Finally, a drop of 0.5 wt% Nafion suspension was covered on the electrode top to prevent the damage of the electrocatalyst layer.

Characterization of electrocatalysts: Electrochemical measurements were performed on an IM6e electrochemical workstation (Zahner-Elektrok, Germany). A standard three-electrode cell with separate anode and cathode compartments was used. A platinum foil and SCE electrodes were used as counter electrode and reference electrode, respectively. All potentials shown in the figures were against the standard hydrogen electrode (SHE). Structural and surface morphologic characterizations of the electrocatalysts were conducted by X-ray diffraction (D/Max-III A diffractometer, Rigaku Co., Japan) using $\text{Cu K}\alpha_1$, $\lambda = 1.54056 \text{ \AA}$ as the radiation source, high-resolution transmission electron microscopy (HRTEM, JOEP JEM-2010, JEOL Ltd.) and scanning electron microscopy (SEM, LEO 1530VP, Germany) in conjunction with energy dispersive X-ray spectroscopy (EDX). The distribution of the metal

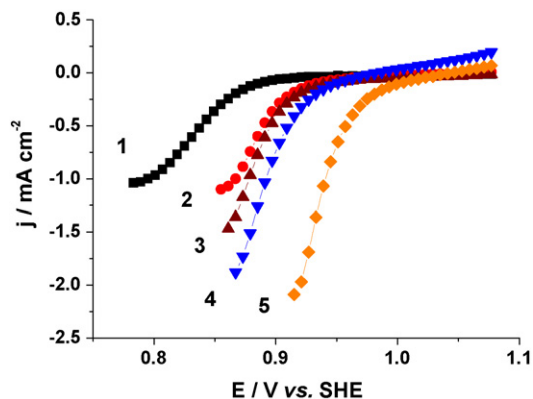


Fig. 1. Linear sweep curves of oxygen reduction on different electrodes in O_2 saturated 1.0 M KOH solution at 25°C . The metal loadings in electrodes are curve 1, $20 \mu\text{g Au}$, curve 2, $20 \mu\text{g Pt}$; curve 3, $20 \mu\text{g Pd}$, curve 4, $20 \mu\text{g Pd} + 20 \mu\text{g WC/C}$ and curve 5, $6.7 \mu\text{g Au} + 6.7 \mu\text{g Pd} + 6.7 \mu\text{g WC/C}$; sweep rate: 2 mV s^{-1} .

components on the support was determined on a QUAUNTA400 (FEI, The Netherlands)/INCA/HKL thermal field emission environment scanning electron microscope (FESEM).

3. Results and discussion

Fig. 1 presents the linear sweep curves of oxygen reduction on different electrodes. The ORR on Au/C electrode shows a higher overpotential than that on Pt/C electrode. The Pd/C electrode shows slightly better performance than Pt/C electrode at the same conditions. Enhancing further the catalytic activity of Pd for ORR is achieved by using nanocrystal tungsten carbide as support (curve 4 in Fig. 1). However, the ORR on AuPd–WC/C electrode shows an over 70 mV shift towards more positive potentials compared with Pt/C electrode even the total metal loading was lower (curve 5 in Fig. 1). The electrocatalytic specific activities were measured at 0.9 V with respect to the normal hydrogen electrode, where the reaction can be considered to occur within the kinetic controlled region [21,22].

The curve of AuPd–WC/C shows a surprisingly high current level of over 100 A g^{-1} metal (Au + Pd) at 0.9 V versus SHE. Moreover, the catalytic current of the AuPd–WC/C electrode rises much more sharply at a more positive potential, which will directly improve the cell efficiency. The result is competitive with the data reported by Joo et al. [23], in which ORR was performed on a rotating disk electrode coated with Pt supported on ordered nanoporous carbon at 10,000 rpm with a scan rate of 50 mV s^{-1} .

In fact, we also measured the performance of the AuPd–WC/C electrocatalyst in acidic solution (Fig. 2). In acidic solution, the activity of Au/C for oxygen reduction is poor. AuPd–WC/C electrocatalyst is very active, however, the increase in the activity for oxygen reduction on AuPd–WC/C electrocatalyst against the Pt/C electrocatalyst is not so significant compared to that in alkaline solution. The onset potentials for oxygen reduction on both AuPd–WC/C electrocatalyst and Pt/C electrocatalyst are almost the same in acidic solution even the reduction current density is higher on the former electrocatalyst than that on the later electrocatalyst.

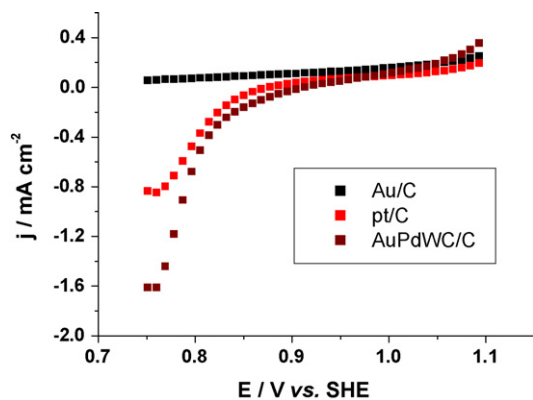


Fig. 2. Linear sweep curves of oxygen reduction on different electrodes in O_2 saturated 1.0 M H_2SO_4 solution at 25 °C. The metal loadings in electrodes are curve 1, 20 μg Au, curve 2, 20 μg Pt; curve 3, 6.7 μg Au + 6.7 μg Pd + 6.7 μg WC/C; sweep rate: 2 mV s^{-1} .

Fig. 3 shows the TEM images of both the tungsten carbide and Au–Pd on tungsten carbide electrocatalyst. As shown, the spherical AuPd particles on carbon are uniform and well distributed. Based on the measurements of 300 particles in random regions, the average particle size was estimated to be 6.9 nm. The results of elemental analysis on these small black dots by EDX are shown in the insets of the corresponding figures. The EDX analysis of the AuPd–WC/C electrocatalyst proved the coexistence of Au, Pd and WC (inset in Fig. 3b). The average particle size ranges between 3.0 and 6.5 nm with the maximum close to 4.9 nm. This is shown in the histogram of particle size distribution (Fig. 3c). It exhibits the features of a Gaussian distribution. The uniform distribution of these particles combined with their small size leads to a good catalyst as exemplified in the use of these materials for the electrocatalysis of oxygen reduction.

The distribution of the metal components on the support was further determined on a QUAUNTA400 (FEI, The Netherlands)/INCA/HKL thermal field emission environment scanning electron microscope (FESEM). Fig. 4a shows the surface mor-

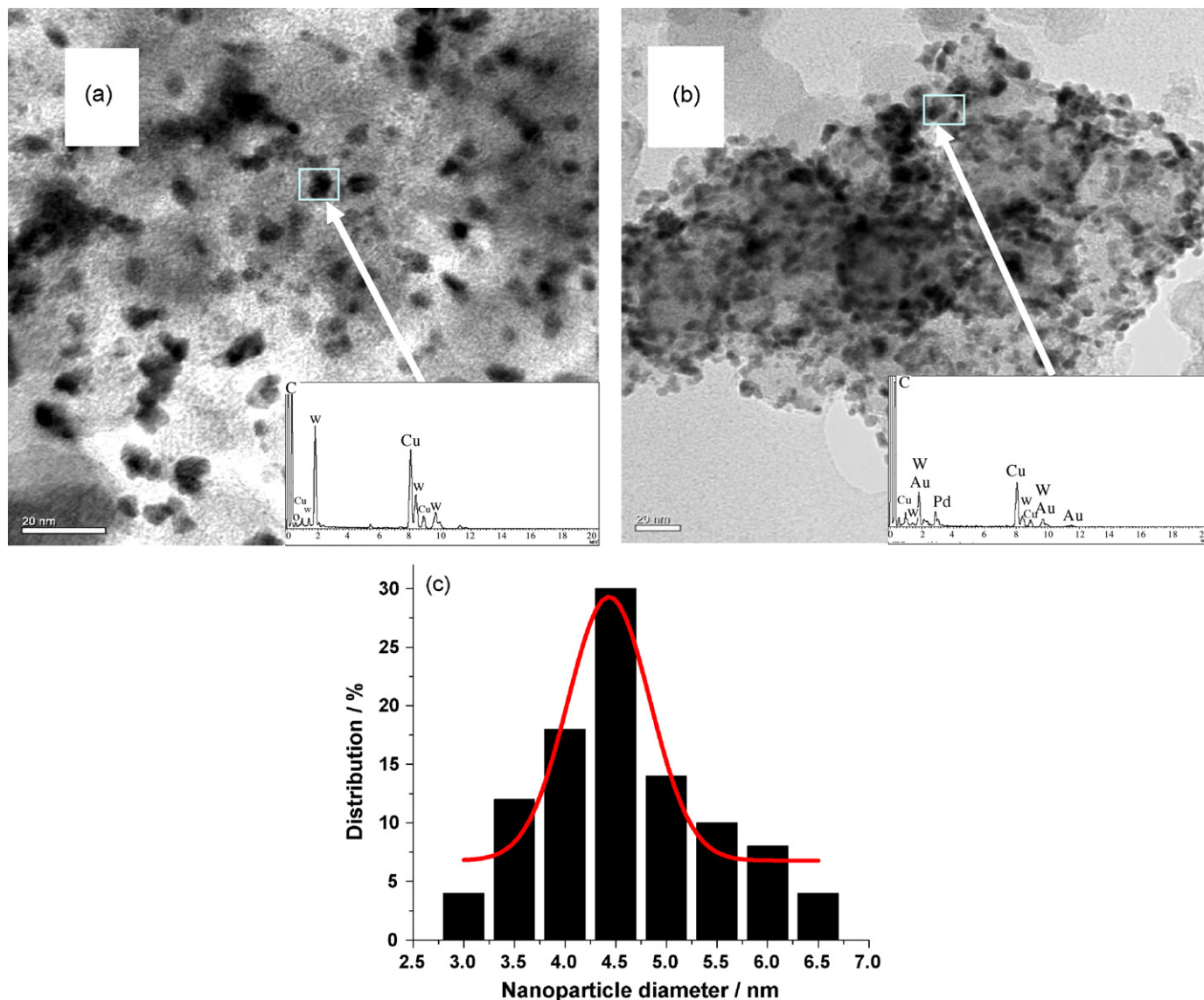


Fig. 3. TEM images and EDX patterns of (a) the tungsten carbide and (b) AuPd–WC/C (bar: 20 nm). (c) Corresponding particle size distribution.

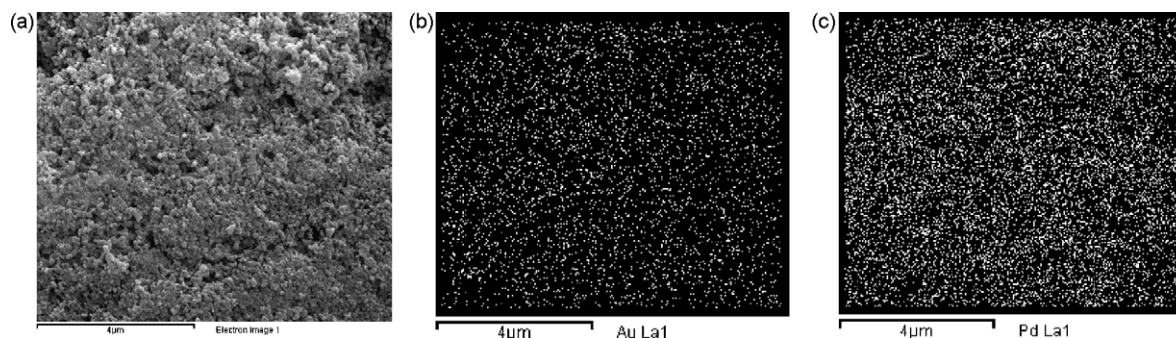


Fig. 4. XRD patterns of four electrocatalysts. The solid lines refer to the 2θ values corresponding to the (1 1 1) and (2 0 0) reflections of single Au and Pd metals.

phology of the AuPd–WC/C electrocatalyst. The typical thermal field emission photographs that show the Au and Pd distribution on the support are shown in Fig. 4b and c. It is clear that both Au and Pd are uniformly distributed on the support.

The XRD determination confirmed that the tungsten carbides and the Au–Pd supported on tungsten carbide by direct reduction are crystals. One of the possible explanations why the activity of oxygen reduction on AuPd electrocatalyst is higher than that on Au or Pd electrocatalyst is the interaction between Au and Pd. The structural characterization of the bimetallic electrocatalyst showed the shifting of the marked peaks for both metals (Fig. 5). The (1 1 1) peaks and (2 0 0) peaks of Au and Pd are almost merged together for AuPd/C and AuPd–WC/C electrocatalysts, indicating the alloying of Au with Pd. However, the degrees of the alloying have not been calculated due to lack of data since it depends on the ratio of Au to Pd, the heating time and the temperature and the structural change. Further work will focus on the study of the factors affecting the degree of alloying.

The mechanism of the enhancement in the activity for oxygen reduction on AuPd–WC/C electrocatalyst is not clear at this stage. The alloying of Au and Pd should be important [1,2]. It

possibly influences the electron distribution and structure, particularly, on the surface of the electrocatalyst which affects the interaction between oxygen molecular and metal. The presence of the WC as support enhances the catalytic activity since WC has the electron distribution similar to that of Pt, indicating a synergistic effect [24].

4. Conclusion

This study demonstrated the preparation of Pt alternative Au–Pd alloy components supported on nanocrystalline tungsten carbide. We showed these novel electrocatalysts could offer the activities that surpass that of the state-of-the-art Pt-based electrocatalysts for oxygen reduction reaction. The advantage seemed to come from the novel support of tungsten carbide which itself has the catalytic activity to enhance the catalytic activity of the metal electrocatalysts. The electrocatalysts that can eliminate the use of the costive Pt but with the enhanced activity towards the ORR could be potentially adopted to reduce the cost of fuel cells.

Acknowledgements

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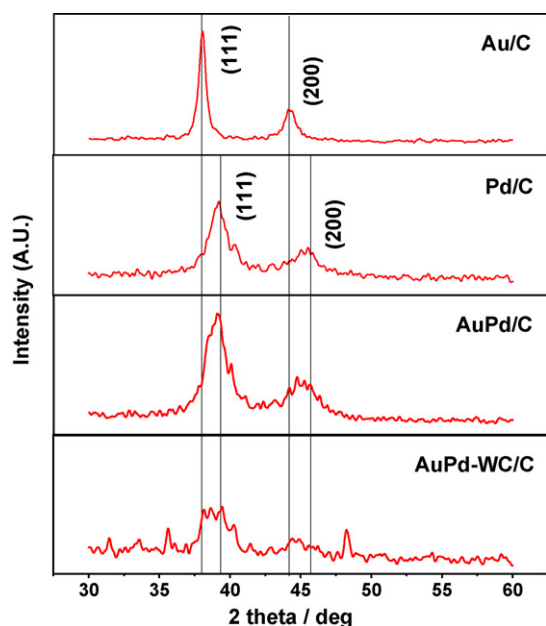


Fig. 5. (a) SEM photograph of AuPd–WC/C electrocatalyst, EDX mapping images of (b) Au and (c) Pd. All the bars are 4 μm .

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