One-step synthesis of AuPd alloy nanoparticles on graphene as a stable catalyst for ethanol electro-oxidation

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ABSTRACT

Room-temperature-ionic-liquid-assisted sputtering with an alloy target is utilized to synthesize the graphene-supported AuPd alloy nanoparticles, whose Au-to-Pd ratio can be well controlled. The preparation process is one-step, free of additives and stabilizers. For direct electro-oxidation of ethanol in alkaline media, the supported AuPd alloy nanoparticles show much higher catalytic activity compared with a commercial Pd/C catalyst and the monometallic counterpart. The optimal Au-to-Pd ratio is 1:3, and the nanocatalyst of AuPd (1:3) possesses high stability and durability. After 500 cyclic voltammetry test cycles, the anodic peak current density for ethanol electro-oxidation still remains about 91% of the initial one. Furthermore, by quantitatively analyzing the relative reactivity retention, the alloy nanoparticle catalysts with graphene as the support show much higher anti-poisoning performance than the corresponding monometallic catalysts with active C as the support.

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Introduction

Direct alcohol fuel cells (DAFCs), a type of alkaline fuel cells (AFC), are one of most promising energy conversion technologies that has attracted much attention in the recent decades [1–3]. The direct oxidation of methanol in fuel cells has been extensively investigated, though there are still some critical issues to be addressed, such as toxicity, environmental problems in relation to the miscibility of methanol to water [3]. Ethanol, which is the major renewable biofuel from fermentation of biomass and can be produced in large quantities from agricultural products, offers an attractive alternative as a fuel in low-temperature fuel cells. Direct ethanol fuel
cells (DEFCs) show high energy-conversion efficiency, low operation temperature and simple handling of the fuel, as well as convenience to use [4–6]. Based on the foregoing works, the selective of ethanol to CO₂ is relatively low, and the ethanol oxidation in alkaline media follows mechanisms below:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} + 3\text{OH}^- &\rightarrow \text{CH}_3\text{CO}_\text{ads} + 3\text{H}_2\text{O} \quad (1) \\
\text{OH}^- &\rightarrow \text{OH}_\text{ads} + e \quad (2) \\
\text{CH}_3\text{CO}_\text{ads} + \text{OH}_\text{ads} &\rightarrow \text{CH}_3\text{COOH} \quad (3) \\
\text{CH}_3\text{COOH} + \text{OH}^- &\rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \quad (4)
\end{align*}
\]

According to Eqs. (1)–(4), the rate-determining step in the ethanol oxidation reaction is Eq. (3) [4,6]. In addition, the catalytic activity of catalysts strongly depends on the pH value of electrolytes, and it is much stronger in alkaline media than in acidic ones. The reason of improved kinetics in alkaline media is that continued dehydrogenation of ethanol cannot readily proceed in acidic media due to the lack of OH species, which can instantly remove hydrogen [7,8]. Meanwhile, the stability, which is related to the structure, morphology and composition of catalysts, is an important factor as well for practical applications of DAFCs.

As we know, Pt-based and Pd-based alloys are widely used as catalysts in DAFCs due to their high catalytic performance [9–14]. However, high cost of Pt is a serious drawback for the commercialization of Pt-based fuel cell technology. In addition, another critical issue for Pt catalyst is less stability, showing up as attenuation fast of catalytic activity in current density-time (i-t) curve, due to the catalyst poisoning arising from the intermediate product [12,15]. Therefore, the development of Pt-free catalysts for fuel cells has been a hot topic in new energy investigations. It is noteworthy that naturally abundant Pd often shows higher catalytic activity than Pt in an alkaline electrolyte for electrocatalytic oxidation of ethanol [16]. Furthermore, forming Pd-based bimetallic catalysts, such as PdNi [17], PdCo [18,19], PdAg [20] and PdCu [21] alloys, can further enhance the catalytic activity and stability of Pd catalysts. In particular, AuPd bimetallic nanoparticles (NPs) have been demonstrated to possess enhanced catalytic activity for ethanol oxidation [22–24]. The improvement upon the addition of Au is attributed to the synergistic effect between two elements, such as ligand effect and ensemble effect [25–27]. The ligand effect refers to the electronic interactions between two components, and the ensemble effect is related to surface atomic arrangements and dilution. Both the effects are associated with the chemical composition and geometric shape of catalysts, and thus it is of great significance to effectively control their compositional ratio and morphology [27]. Moreover, an alternative approach can also be adopted to improve the activity and anti-poisoning performances of catalysts, normally called employing suitable supports.

Graphene is a one-atom-thick two-dimensional sheets of graphite with p-electrons fully delocalized on the graphite plane with a number of unusual properties, such as high thermal conductivity and mechanical stiffness, extraordinary electronic transport properties, and high specific surface area, to stabilize nanocatalysts such as metal NPs [28–31]. Because catalysis is a surface effect, catalysts often need to have a surface area as high as possible. The graphene-supported nanocatalysts can offer not only a high surface area but also a conductive surface, which is beneficial for electron transport in many catalytic processes. It has been demonstrated in the Pt-based and Pd-based NPs catalysts grown on graphene for electrocatalytic reactions [10,11,15]. Recently, Wang et al. proved that the metallic NPs supported on the surface of graphene show superior anti-poisoning performance for formate oxidation [32]. Therefore, it is necessary to combine the metallic NPs catalysts with graphene support toward the ethanol oxidation for high activity and superior anti-poisoning performance.

Recently, we developed an alternative approach to prepare graphene-supported AuPd alloy NPs by successively sputtering Au and Pd onto room temperature ionic liquids (RTILs), e.g. 1-butyl-3-methylimidazolium tetrafluoroborate [BMIm][BF₄] [33–36]. It is a universal and environmental-friendly method totally free of such as reducing and stabilizing agents. On the basis of the foregoing research, we extend this means to prepare AuPd alloy NPs on graphene straightforwardly from alloy targets with different Au-to-Pd ratios. The catalytic activities of graphene-supported AuPd alloy NPs show a strong dependence on the Au-to-Pd ratio, suggesting occurrence of the synergistic effects. Moreover, the nanocatalyst with an optimal composition of AuPd (1:3) exhibits much superior catalytic activity and stability for ethanol electro-oxidation.

Materials and methods

Materials

All chemicals used in this study were in analytical grade. Ethanol and KOH were purchased from Alfa Aesar and used as received. Graphene powder was purchased from Nanjing XFNANO Materials Tech, which is prepared by the thermal exfoliation reduction and hydrogen reduction. [BMIm][BF₄] (purity > 99%) was purchased from Shanghai Cheng-Jie Chemical and purified in vacuum for 24 h before using. Double-distilled water was used for the preparation of standard solution.

Preparation of graphene-supported metal NPs

As reported in our previous articles [33–35], the Au, Pd and AuPd alloy NPs were prepared via a RTIL-assisted sputtering deposition process. We replace the monometallic targets by AuPd alloying targets with different Au-to-Pd ratio to achieve uniform component ratios in the sputtered nanostructures. First, 10 mg graphene powder was fully dispersed into 1.5 ml [BMIm][BF₄] with ultrasonication for 10 min. Then, the black graphene-RTIL suspension was dropped into a clean stainless steel pot, and the metal of interest was sputtered onto the graphene-RTIL suspension at room temperature for 600 s in a desktop direct-current sputtering system (Quorum Technologies, equipped with a thickness monitor which is calibrated by a surface profiler). Eventually, the alloy NPs and monometallic NPs were separated from [BMIm][BF₄] with high-speed centrifugation and decantation, followed by washing
in an ultrasonic bath of acetone. This cleaning process was repeated several times to completely remove residual [BMIm][BF₄] from the graphene supported NPs hybrids (in dry powder form).

**Characterization of graphene-supported metal NPs**

The microscopic structures of the graphene-supported AuPd alloy NPs were characterized with high-resolution transmission electron microscopy (HRTEM, FEI Quanta FRG 200F, operating at 200 kV) and high-angle annular dark-field scanning TEM (HAADF-STEM). The crystalline structures of graphene-supported AuPd alloy NPs were characterized with X-ray diffraction (XRD, PANalytical Empyrean). The electronic structures of graphene-supported AuPd alloy NPs were characterized with X-ray photoemission spectroscopy (XPS, Kratos Axis Ultra DLD, monochromatic Al Kα) in ultrahigh vacuum. The inductive coupled plasma-atomic emission spectroscopy (ICP-AES) measurements were conducted with Varian Vista MPX, and the samples were digested in concentrated HNO₃ and then diluted to desired concentrations.

**Electrochemical measurements**

The electrochemical activities of the graphene-supported AuPd alloy NPs and commercial Pd/C (20 wt%; Sigma) catalysts were characterized by cyclic voltammetry (CV) and chronoamperometry (CA) techniques. The measurements were performed with a three-electrode cell in a CHI660E electrochemical workstation at ambient temperature. Typically, the catalyst dispersion was prepared by mixing 5 mg of catalysts in 2 ml of solution containing 2 ml of ethanol and 20 μL of 5 wt% Nafion solution followed by ultrasonication for 30 min. Glassy carbon (GC) electrode (3 mm in diameter) served as the substrate for the catalysts. Prior to use, the GC electrode was polished using aqueous alumina suspension, and then 10 μL aliquots of catalysts suspension was pipetted with a micropipettor onto the GC surface. An Ag/AgCl electrode and a Pt wire were used as the reference electrode and the counter electrode, respectively. The electrochemistry tests were carried out in an aqueous solution containing 1 mol/L potassium hydroxide (KOH) and 1 mol/L ethanol (C₂H₅OH), sweeping from −0.8 to 0.2 V at a scan rate of 50 mV/s. All potentials herein are relative to Ag/AgCl electrode, and all the electrochemical measurements are conducted at 25 °C in a N₂-saturated solution.

**Results and discussion**

As illustrated in Fig. 1, the microscopic structures of the graphene-supported Pd NPs and Au NPs are characterized with TEM and HRTEM. The supported Pd NPs shown in Fig. 1a and b have uniform size, around 2.54 nm. An identical interplanar spacing of 0.23 nm is present in the HRTEM image, indicating the crystallinity of the (111) lattice plane for face-
centered cubic (fcc) Pd. As for the supported Au NPs shown in Fig. 1c and d, the average size of Au NPs, up to 6.68 nm, is much larger than that of Pd NPs. The interplanar spacing of 0.23 nm corresponds to the (111) lattice plane of fcc Au [22,24]. The morphology of the Au and Pd NPs is quite different under the same preparation conditions, which may be associated with the extent of the interaction between RTILs and different kinds of metal NPs [33,37,38].

The TEM and HRTEM images of the graphene-supported AuPd alloy NPs with different Au-to-Pd ratios are shown in Fig. 2. Three AuPd alloy targets for the sputtering, with Au-to-Pd mole ratios of 3:1, 1:1 and 1:3, are selected for the sputtering. For AuPd (3:1) shown in Fig. 2a and b, the size distribution of NPs is not uniform, where the average diameter is about 4.51 nm. On the other hand, for AuPd (1:1), depicted in Fig. 2c and d, the size distribution of AuPd NPs becomes more uniform and narrow. In this case, the average diameter is 2.55 nm, which is much smaller than that of AuPd (3:1). With an increase of Pd content to AuPd (1:3), the average diameter of AuPd NPs is further reduced to 2.10 nm, as shown in Fig. 2e and f. All the samples show a same lattice spacing of 0.23 nm, which is similar to the monometallic NPs shown in Fig. 1.

To probe the microscopic structure for AuPd NPs, HADDF-STEM is utilized to study the elemental spatial distribution.
The crossline profiles of the elemental composition for AuPd NPs with different Au-to-Pd ratio are shown in Fig. 3a, b and c, corresponding to AuPd (3:1), AuPd (1:1) and AuPd (1:3), respectively. The green and orange curves represent Au and Pd, respectively. There is a coexistence of both metal species in the NPs, indicating that the occurrence of local alloying. Considering that the preparation process is one-step sputtering deposition from the AuPd alloy targets, the formation of AuPd alloy NPs on graphene is reasonable. Furthermore, the energy dispersive spectroscopy (EDS) analysis shown in the insets in Fig. 3 suggests that the Au-to-Pd atomic ratios are close to the corresponding nominal composition predetermined in the alloy targets. The real percentages of Au and Pd are evaluated with ICP-AES. For AuPd (1:3), AuPd (1:1) and AuPd (3:1), the Au-to-Pd atomic ratios derived from ICP-AES are about 24:76, 44:56 and 77:23, respectively, which are highly consistent with those in the alloy targets. Therefore, it is easy and controllable to prepare AuPd alloy NPs with a precise Au-to-Pd ratio by employing the present RTILs-assisted sputtering method.

The XRD patterns of the metal NPs are shown in Fig. 4, where the crystalline features of Au (111), (200), (220), (311) and (222) are clearly present. However, the diffraction peaks of Pd are weak with a broad full-width at half-maximum (FWHM), owing to tiny size of Pd NPs. In the case of AuPd (3:1), all the diffraction peaks are shifted upward slightly compared to Au NPs. Meanwhile, peak FWHM for AuPd (3:1) are broadened as

**Fig. 3** – HAADF-STEM images and crossline profiles of elemental composition (based on EDS data) for graphene-supported AuPd alloy NPs with different Au-to-Pd ratios: (a) for 3:1; (b) for 1:1; and (c) for 1:3.

**Fig. 4** – XRD patterns of graphene-supported AuPd (3:1), AuPd (1:1) and AuPd (1:3) alloy NPs, and of Au and Pd monometallic NPs as references.

The crossline profiles of the elemental composition for AuPd NPs with different Au-to-Pd ratio are shown in Fig. 3a, b and c, corresponding to AuPd (3:1), AuPd (1:1) and AuPd (1:3), respectively. The green and orange curves represent Au and Pd, respectively. There is a coexistence of both metal species in the NPs, indicating that the occurrence of local alloying. Considering that the preparation process is one-step sputtering deposition from the AuPd alloy targets, the formation of AuPd alloy NPs on graphene is reasonable. Furthermore, the energy dispersive spectroscopy (EDS) analysis shown in the insets in Fig. 3 suggests that the Au-to-Pd atomic ratios are close to the corresponding nominal composition predetermined in the alloy targets. The real percentages of Au and Pd are evaluated with ICP-AES. For AuPd (1:3), AuPd (1:1) and AuPd (3:1), the Au-to-Pd atomic ratios derived from ICP-AES are about 24:76, 44:56 and 77:23, respectively, which are highly consistent with those in the alloy targets. Therefore, it is easy and controllable to prepare AuPd alloy NPs with a precise Au-to-Pd ratio by employing the present RTILs-assisted sputtering method.

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**Fig. 5** – (a) XPS Au 4f spectra and (b) Pd 3d spectra for graphene-supported AuPd (3:1), AuPd (1:1) and AuPd (1:3) alloy NPs, and of Au and Pd monometallic NPs as references, respectively.
well, which can be ascribed to the size reduction of AuPd NPs. Upon increased addition of Pd, the diffraction patterns for AuPd (1:1) and AuPd (3:1) are similar to those of Pd monometallic NPs. Significantly, as demonstrated in Fig. 4, the Au (111) peak shifts toward the Pd (111) peak when decreasing the Au-to-Pd ratio, supporting the argument of the formation of AuPd alloy NPs [24,39–42].

The surface chemistry of the supported metal NPs is characterized by XPS, and the Au 4f and Pd 3d core level spectra are shown in Fig. 5. The two peaks in Fig. 5a can be assigned to the Au 4f7/2 and 4f5/2 states of zero-valent Au. The binding energies of Au 4f7/2 for Au-only, AuPd (3:1), AuPd (1:1) and AuPd (1:3) are 84.0, 84.0, 83.9 and 83.8 eV, respectively, which decrease with increasing the Pd content. The binding energy shift implies the charge transfer between Au and Pd. On the other hand, as demonstrated in Fig. 5b, the shoulder peak (~337.5 eV) at higher binding energy of Pd 3d5/2 is decreased upon increasing Au-to-Pd ratio. As the shoulder peak arises from oxidative Pd, the dilution of Pd by Au can suppress surface oxidation of Pd and improve its air stability [22,35,43]. The XPS results are in good agreement with the microscopic and crystalline characterization, indicating the occurrence of alloying in the supported AuPd NPs.

In order to study the synergistic effect in the AuPd alloy NPs, whose catalytic activity for ethanol electro-oxidation in an alkaline electrolyte is evaluated and compared with a commercial Pd/C catalyst. Fig. 6a shows the CV curves with two featured oxidation peaks during a round scan. The oxidation peak in the forward scan can be attributed to the oxidation of the chemisorbed species arising from ethanol adsorption, while the oxidation peak in backward scan can refer to the removal of the carbonaceous species which are not completely oxidized in forward scan. The derived specific activity for AuPd (1:3) is 186 mA/cm², which is much higher than 70 mA/cm² for commercial Pd/C and 81 mA/cm² for AuPd (1:1) and 81 mA/cm² for AuPd (3:1). In addition, the onset potential of AuPd (1:3) is about –0.68 V which is lower than that of commercial Pd/C. The results demonstrate the enhancement in catalytic activity for ethanol electro-oxidation upon alloying of Au and Pd with an appropriate Au-to-Pd ratio.

As shown in Fig. 6b, the operational stability of the catalysts is tested by the long-term CA measurements. The current decay for the AuPd alloy NPs is significantly slower than that for commercial Pd/C, indicating their better endurance in the ethanol electro-oxidation reaction. Furthermore, the residual current of AuPd (1:3) is larger than those of commercial Pd/C and the other compared catalysts, confirming the highest catalytic performance for AuPd (1:3).

It has been known that the addition of Au into Pd catalysis can enhance catalytic activity and selectivity as well as the resistance to poisoning, which also can summarize from CA and CV results in Fig. 6. Wang et al. propose a new method, relative reactivity retention (RRR) values, to quantitatively assess the anti-poisoning performance of anode catalysts via evaluating CA currents with reference to CV currents [32]. The RRR is defined as $I_{CA}/I_{CV}$, where the $I_{CA}$ refers to the CA current at certain time point while $I_{CV}$ refers to the corresponding CV current at $-0.25$ V obtained from the forward scan curves. Therefore, a higher RRR value for a catalyst means a higher anti-poisoning performance. From the Table 1 we can see that the RRR values of Pd-based NPs supported on graphene are all far larger than that of commercial catalysts, which is supported on active carbon (5.7% at 3500 s), indicating superior anti-poisoning effect of as-prepared catalysts supported on graphene than on active carbon. Meanwhile, compared with Pd-graphene (16.1% at 3500 s), all AuPd alloy NPs catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$I_{CA}$/mA/cm²</th>
<th>500 s</th>
<th>1500 s</th>
<th>2500 s</th>
<th>3500 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuPd 1:3</td>
<td>69.8</td>
<td>54.4</td>
<td>44.5</td>
<td>36.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RRR/%</td>
<td>57.5</td>
<td>44.8</td>
<td>36.7</td>
<td>30.1</td>
</tr>
<tr>
<td>AuPd 1:1</td>
<td>43.4</td>
<td>25.8</td>
<td>18.7</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RRR/%</td>
<td>65.3</td>
<td>38.8</td>
<td>28.1</td>
<td>22.2</td>
</tr>
<tr>
<td>AuPd 3:1</td>
<td>23.3</td>
<td>17.1</td>
<td>13.7</td>
<td>12.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RRR/%</td>
<td>50.2</td>
<td>36.8</td>
<td>29.5</td>
<td>26.5</td>
</tr>
<tr>
<td>Pd-G</td>
<td>34.9</td>
<td>18.9</td>
<td>13.7</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RRR/%</td>
<td>50.1</td>
<td>29.7</td>
<td>21.5</td>
<td>16.1</td>
</tr>
<tr>
<td>Pd/C</td>
<td>10.1</td>
<td>5.2</td>
<td>3.5</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RRR/%</td>
<td>19.2</td>
<td>9.9</td>
<td>6.7</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Table 1 – A comparison in anti-poisoning performance of supported AuPd alloy NPs and Pd monometallic NPs based upon CA and CV results.
show higher RRR values, further confirming the higher anti-poisoning performance of alloy NPs than monometallic NPs because of the synergistic effect between Au and Pd components.

Fig. 7 shows a comparison of the initial catalytic behavior and that after repeated use. Using the anodic peak current density in forward scan after 10 CV cycles as the reference, the peak current density for AuPd (1:3) retains about 91% of activity after 500 CV cycles. This is much greater than 37% for commercial Pd/C and 46% for the Pd monometallic counterpart. Therefore, the AuPd alloy NPs show higher catalytic stability compared with their monometallic counterparts, which is critical to practical applications for DAFCs.

**Conclusions**

A straightforward approach, by the employment of an alloy target for the RTIL-assisted sputtering, has been developed to prepare the AuPd alloy NPs on graphene. The graphene-supported alloy NPs can act as a catalyst for ethanol electro-oxidation with both high catalytic activity and high stability, which are far superior to the performance of a commercial Pd/C catalyst. The synergistic effect between alloy components and the support effect will enhance the anti-poisoning performance of catalysts. The compositional ratio in the alloy NPs can be controlled simply by the selection of alloy targets, and the optimal Au-to-Pd ratio turns out to be 1:3 in the present work.
case. The current strategy opens a new opportunity to design and tailor the composition of alloy NPs for catalysis and energy applications.

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