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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 [1]. 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

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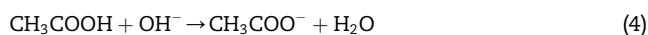
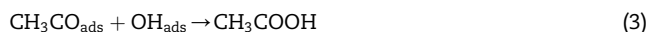
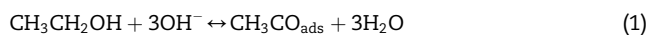
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cells (DEFCs) show high energy-conversion efficiency, low operation temperature and simple handling of the fuel, as well as convenience to use [4–6]. Based on the foregoing works, the selective of ethanol to CO_2 is relatively low, and the ethanol oxidation in alkaline media follows mechanisms below:



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 ratios, 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 XFANO 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

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