



Cu₃P/RGO promoted Pd catalysts for alcohol electro-oxidation

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ABSTRACT

Herein, we reduced PdCl₄²⁻ ions on the synthetized cuprous phosphide/reduced graphene oxidation (Cu₃P/RGO) hybrids to improve the catalytic activity and durability of Pd nanocrystals. In comparison with commercial Pd/C and Pd/RGO catalysts, the Pd/Cu₃P/RGO exhibit high electroactivity and durability toward alcohol oxidation in alkaline medium. The enhanced catalytic performance of Pd/Cu₃P/RGO is due to the high electrochemically active surface area, which can be ascribed to the interactions between Cu₃P/RGO and Pd nanocrystals. The investigation of Cu₃P/RGO as a promoter in alcohol electrooxidation will offer an opportunity in the field of direct alcohol fuel cells (DAFCs).

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1. Introduction

Great efforts have been put forward to develop environment-friendly and high efficiency devices due to the environmental pollution and enormous energy demand of modern society [1,2]. Fuel cells which convert the chemical energy directly to electricity without a mechanical transmission and high pollutant emission are generally considered as an important power source [3,4]. As the potentially excellent direct fuel cells, direct alcohol fuel cells (DAFCs) have attracted particular attention owing to their fewest environmental issues and excellent volumetric energy density [5–8]. Although DAFCs have the widespread application prospect for green energy devices, the value of Pt is the main barrier to the commercialization of DAFCs [9]. Therefore, exploring non-Pt nanocatalysts to reduce costs is necessary. Recently, Pd element has become a promising alternative electrocatalyst to Pt in DAFCs, because of its more abundant in nature, relatively high electrocatalytic activity and durability [10].

It is well-known that supporting materials can affect catalytic activity of electrocatalysts [11,12]. In the current studies, graphene is widely used for dispersing the noble metal to reach better electrocatalytic performance because graphene possesses large surface area, unique electronic properties, high chemical and thermal stability [13,14]. For example, Wang et al. developed a spray-drying

method to synthesize a 3D crumpled graphene. The graphene supported Pd nanocrystals show a higher catalytic surface area, catalytic activity and stability than Pd/RGO and commercial Pd/C toward formic acid electrooxidation [15]. Jiang et al. have developed a facile method to synthesize single-crystalline Pd square nanoplates encased within [100] facets using GO as the template. The fabricated material exhibits a superior catalytic performance for the formic acid oxidation reaction because of the facet effect and large electrochemically active surface area arising from the two-dimension structure [9].

During the past decades, as potentially functional electrode materials, transition metal phosphide materials have aroused great research interest owing to their physical properties including relatively high mechanical strength, electrical conductivity and chemical stability [16,17]. Furthermore, transition metal phosphide materials (such as Ni₂P, CoP, FeP, and Cu₃P) with suitable surface properties can be produced by suitable synthesis procedures and modified conditions, which can efficiently improve the electrocatalytical activity of Pt or Pd toward organic small molecule oxidation. For example, Li et al. use *in situ* nucleation and growth of Pd nanoparticles on the fabricated CoP nanosheets, the obtained catalysts exhibit improved electrocatalytic activity and durability, the enhanced performance can be ascribed to the strong interactions between CoP and Pd nanocrystals [18]. Chang et al. have found that using Ni₂P nanoparticles as a co-catalyst can immensely enhance the catalytical activity and stability of Pd for formic acid electrooxidation [19]. As far as we know, Cu₃P/RGO reinforced hybrid Pd nanocatalysts have not been reported toward alcohol

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electrooxidation.

Herein, we anchored Pd nanoparticles onto Cu₃P/RGO hybrid to improve the electrocatalytic activity and durability of Pd nanoparticles through electrostatic interactions between Pd precursor salt and Cu₃P/RGO hybrids. The obtained Pd/Cu₃P/RGO catalysts display much higher electrocatalytic activity and better durability toward alcohol oxidation in alkaline condition than that of Pd/RGO and commercial Pd/C catalyst. The role of Cu₃P on the enhancement of electrocatalytic performance was also investigated. The fabricated Pd/Cu₃P/RGO nanocomposites may be a promising anodic catalyst applied in the field of DAFCs.

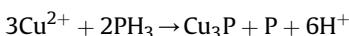
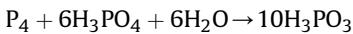
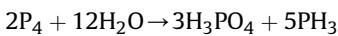
2. Experimental

2.1. Materials

GO was purchased from Nanjing XFNANO Materials Tech Co.,Ltd. CuCl₂·2H₂O, NH₃·H₂O, NaOH, ethylene glycol (EG) were purchased from Sinopharm Chemical Reagent Co., Ltd., China., and phosphorous (P, 97.0%) was obtained from Aladdin Industrial Corporation. All chemicals were of analytical grade and used as received without further purification. Doubly distilled water (18.3 MΩ) was used for all solution preparations. An aqueous H₂PdCl₄ solution was prepared by completely dissolving PdCl₂ powder in HCl solution.

2.2. Synthesis of Cu₃P/RGO

In a standard procedure for the synthesis of Cu₃P/RGO hybrids, GO powder (10 mg) was dispersed in 20 mL water and the mixture was treated by ultrasonic waves for 120 min. Then, the GO suspension, 50 mg of CuCl₂·2H₂O and 20 mL of 28% NH₃·H₂O were placed in a Teflon-lined stainless-steel autoclave, the solution was stirred for 30 min to obtain a homogeneous suspension. After that, 100 mg of phosphorus was added. The autoclave was heated at 413.15 K for 12 h and then cooled to room temperature. The obtained product was separated by centrifugation and washed several times with distilled water. Finally, the as-prepared product was dispersed into 10 mL of water for the next step. The reduction reactions can be described by the following equations [20]:



2.3. Synthesis of Pd/Cu₃P-RGO

In a typical procedure, the aqueous solutions of Cu₃P/RGO (2.5 mL) and H₂PdCl₄ (1 mL of 22.56 mM) were mixed together in 10 mL of EG. Subsequently, the solution was stirred for 30 min to obtain a homogeneous suspension. The pH value of the solution was adjusted to 11 by dropping 0.5 mL NaOH solution. Then the mixed solution was transferred into a Teflon-lined stainless-steel autoclave and heated to 433.15 K. 4 h later, the autoclave was taken out and cooled to room temperature. Finally, the obtained Pd/Cu₃P/RGO suspension was centrifuged and washed several times with water. The product was added into 10 mL of water and dispersed by ultrasonication for 30 min to obtain a homogeneous suspension. Pd/RGO catalyst was prepared in a similar method.

2.4. Apparatus

A TECNAI-G20 electron microscope (TEM) at an accelerating voltage of 200 kV was used to characterize the morphologies of the products. The morphology and composition of the as-prepared catalysts were characterized on a scanning electron microscope (SEM, S-4700, Japan) equipped with an energy dispersive X-ray spectroscopy (EDX, S-4700, Japan). X-ray diffraction (XRD) measurements were performed on a PANalytical X'Pert Pro MPD system with Cu K α radiation source ($\lambda = 1.54056 \text{ \AA}$). The Raman spectra were recorded on a RM2000 microscope by using a 633 nm argon ion laser. X-ray photoelectron spectroscopy (XPS) was performed on a VG Scientific ESCALab 220XL electron spectrometer using 300 W Al K α radiation.

2.5. Electrochemical testing

The electrochemical data were performed using a CHI760E electrochemical workstation (Shanghai CH Instrumental Co.) at room temperature. A conventional three-electrode cell was used, including a platinum wire, a saturated calomel electrode (SCE) and a glassy carbon electrode (GCE, diameter: 3.0 mm). The GCE was carefully polished with alumina slurry on a polishing cloth and then sonicated in double distilled water bath for 10 min before use. The working electrodes were prepared by pipetting 10 μL of the catalyst ink onto the GCE surface and drying at 333.15 K. Assuming a 100% reduction rate for PdCl₄²⁻, the theoretical mass loading of Pd in electrocatalysts was all fixed to be 2.4 μg . The working electrodes were performed by cyclic voltammetry (CV) from -0.9 to 0.3 V at a scan rate of 50 mV s⁻¹ in 1.0 M KOH, 1 M KOH + 1 M CH₃OH and 1 M KOH + 1 M C₂H₅OH solution, respectively. Chronoamperometric curves for methanol and ethanol electrooxidation were also measured in the above solution at -0.21 and -0.25 V, respectively.

3. Results and discussion

The morphologies of Pd/RGO, Cu₃P/RGO and Pd/Cu₃P/RGO hybrids were characterized by SEM. It can be seen in Fig. 1A, most of Pd nanocrystals on the surface of RGO are agglomerate. From Fig. 1B, since so many Cu₃P nanocrystals mixed with RGO, Cu₃P/RGO hybrid exhibit a rough surface, which is benefit to the dispersion of the noble metal. Fig. 1C shows the SEM images of Pd/Cu₃P/RGO hybrid, which reveals that Pd and Cu₃P nanoparticles were uniformly attached to the RGO. To explore the elementary composition of Cu₃P/RGO, Pd/Cu₃P/RGO and Pd/RGO hybrids, the materials were investigated by EDX, and the relevant spectra are shown in Fig. 1D, E and F. The C and O elements are assigned to RGO, Cu and P elements are assigned to Cu₃P. The Pd peak is shown in Fig. 1D and F, demonstrating that Pd presents as the component element in the prepared catalysts. Furthermore, the element distributions of the as-prepared Pd/Cu₃P/RGO hybrids were determined by element mapping, as shown in Fig. S1.

The morphologies of Pd/RGO, Cu₃P/RGO and Pd/Cu₃P/RGO catalysts were also characterized by TEM. As shown in Fig. 2A, the Pd nanocrystals are distributed on the RGO surface. Fig. 2B confirms the formation of Cu₃P/RGO, and Fig. 2C show that the Pd nanocrystals were dispersed on the surface of Cu₃P/RGO. The mean diameters of Pd nanoparticles in the Pd/RGO and Pd/Cu₃P/RGO hybrids were estimated and shown in Fig. S2. From the histograms, the average diameters of Pd nanoparticles in Pd/Cu₃P/RGO and Pd/RGO hybrids are approximately 9.8 nm and 14.7 nm, respectively.

Fig. 3 presents the XRD patterns of Pd/RGO, Cu₃P/RGO and Pd/Cu₃P/RGO catalysts. The red and black vertical lines represent the diffraction peak characteristics of the Pd (JCPDS card No. 87-0645) and Cu₃P (JCPDS card No. 74-1067), respectively. In the XRD

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