



Enhanced electrocatalytic performance on polymer-stabilized graphene decorated with alloy nanoparticles for ethanol oxidation reaction in alkaline media



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ABSTRACT

We explore a green method to grow metal alloy nanoparticles (NPs) on reduced graphene oxide stabilized with polyvinylpyrrolidone (PVP) in aqueous solution with sodium borohydride as a reducing agent for metal ions. PVP was used to stabilize nano-graphene sheets (NGs) in solution and prevent their aggregation. The synthetic experimental conditions were studied to control the size, shape and distribution of alloy nanoparticles anchored on the graphene sheets. AuPt nanoparticles on PVP-stabilized graphene (PVP-NGs-AuPt) show higher catalytic activity and stability than those on graphene without PVP (NGs-AuPt) toward the ethanol oxidation reaction (EOR) in alkaline media. PVP-NGs-AuPt can increase the EOR peak current density by more than 160%, ~100% and 78% as compared with Pt on carbon, AuPt on carbon and NGs-AuPt, respectively. Moreover, the poisoning of PVP-NGs-AuPt during the EOR is less significant than that of NGs-AuPt, as revealed by analyzing the intermediates products, acetate and carbonate, by ion exchange chromatography. The high electrocatalytic activity of PVP-NGs-AuPt is attributed to the surface activation by OH⁻ and the interaction between the AuPt NPs and graphene, which can improve the CO oxidation within the applied potential range.

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1. Introduction

Direct alcohol fuel cells convert chemical energy into electricity in high energy conversion efficiency. Alcohols have high energy density and are readily available. It is convenient to transport and store alcohols. But there are a couple of challenges to overcome for the commercialization of direct alcohol fuel cells on a large scale. A key issue is to select appropriate electrode–fuel combinations in acidic or alkaline medium [1–3]. The major hurdle for the commercialization of direct alcohol fuel cells lies in using the precious Pt with high loading as the electrocatalyst [2–5]. Although Pt is a very effective catalyst for the oxygen reduction at cathode and the alcohol oxidation at anode [6–8], it is a rare metal and very expensive [4,5]. In addition, the Pt surface can be readily poisoned by adsorbed CO. In order to overcome these issues, Pt nanoparticles (NPs) and its alloy NPs have been investigated as the electrocatalyst of fuel cells. The Pt loading can be lowered and its catalytic activity can be greatly increased by alloying with Au. Because Au is more electronegative than Pt, electrons transfer from Pt atoms

into Au atoms in PtAu alloy. This electron transfer can improve the catalytic activity. In addition, the negatively charged Au atoms can facilitate the oxygen supply, leading to the complete oxidation of ethanol and prohibition of the building up of CO_{ads} on the catalyst surface. Hence, AuPt NPs have been studied as the electrocatalysts for many energy conversion-related chemical reactions, including the low molecular weight alcohol oxidation, formic acid oxidation, formaldehyde oxidation, ethylene glycol oxidation and oxygen reduction [9–19]. It was observed that the AuPt alloy NPs have remarkably higher catalytic activity than Pt. Apart from the alloying effect, the supporter of metal NPs can also significantly affect the electrocatalytic activity [20]. The requirements for the supporter include high surface area, suitable porosity for ion transport and high electrical conductivity. Conventionally, carbon such as Vulcan XC-72 (carbon black, XC-72) is popular as the supporter because of its large surface area, relatively good electrical conductivity and high porosity [21]. But the surface area of carbon blacks is mainly due to the micropores of less than 1 nm. These micropores are difficult to fully access for electrolyte, so that they make little contribution to the catalysis [22]. Graphene has received considerable attention as the replacement of carbon black as the supporter for nanocatalyst [23–34]. It has a theoretical surface area of about 2600 m² g⁻¹ and a high electrical conductivity of 10⁵–10⁶ S m⁻¹. It

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has been reported that the graphene supporter can greatly improve the catalytic activity of Pt [35,36]. For example, Pt nanoparticles on graphene have much higher electrocatalytic activity for methanol oxidation than on carbon. Pt and bimetallic Pt alloy on graphene have been investigated as the electrocatalysts for the methanol oxidation, formic acid oxidation and oxygen reduction reactions [12,35–43]. In order to prevent the stack up of the graphene sheets, polymers were also adopted. However, metal alloy NPs on graphene have been rarely explored for the ethanol oxidation reaction (EOR). To the best of our knowledge, there is no report on investigating AuPt alloy nanocatalysts on graphene for EOR. Ethanol as a nontoxic liquid and easily available fuel has higher energy density than methanol and formic acid. But much more research work is needed for direct ethanol fuel cells as EOR is much more complicate than the oxidations of methanol and formic acid. In this study, we present a facile approach to grow AuPt alloy NPs on polyvinylpyrrolidone (PVP)-stabilized graphene. PVP can stabilize graphene in solvent, because it can be adsorbed on the surface of graphene [44]. AuPt alloy NPs on PVP-stabilized graphene (PVP-NGs-AuPt) exhibit significantly higher electrocatalytic activity than those without PVP toward EOR in alkaline media.

2. Experimental

2.1. Materials

Highly pure natural graphite powder (SP-1 graphite, purity >99.99%) with an average particle size of $\sim 30 \mu\text{m}$ was purchased from the Bay Carbon Inc. Other chemicals, including PVP (MW = 50,000–60,000), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 5 wt% Nafion ionomer solution, 2-propanol, KMnO_4 , NaBH_4 , NaNO_3 , H_2O_2 , H_2SO_4 , NaOH , ethanol, hydrazine hydrate and HCl , were supplied by Sigma–Aldrich with the analytical grade purity. All the chemicals were used as received without any further purification.

2.2. Synthesis of PVP-stabilized graphene sheets

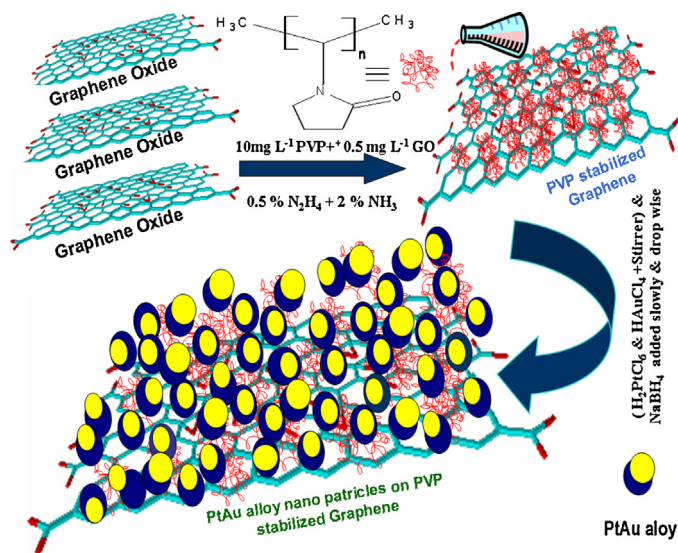
Graphene was prepared by the reduction of graphene oxide (GO). GO was synthesized according to the modified Hummer's method [45–47]. 60 mL of 10 mg mL^{-1} PVP solution was mixed with 30 mL of 0.5 mg mL^{-1} GO solution. The PVP/GO solution was vigorously stirred for more than 10 h. Then, 1 mL of 0.5 wt% hydrazine solution and 3 mL of 2% ammonia solution were added, and the mixture was stirred for 2 h at 100°C . The black precipitate, reduced graphene oxide, was collected by vacuum filtration with 200 nm membrane filter paper. It was then washed with deionized-water for several times. Finally, the graphene sheets stabilized with PVP (NGs-PVP) were successively desiccated with a freeze-dryer for 2 days.

2.3. Growth of nanoparticles on PVP-NGs

AuPt NPs were prepared through the simultaneous reduction of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ aqueous solution with NaBH_4 at the presence of an appropriate amount of NGs-PVP (Scheme 1) [48]. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ had the same weight concentration in the solution. Control catalysts, Pt nanoparticles on XC-72 (C-Pt), Pt nanoparticles on graphene (NGs-Pt) and AuPt nanoparticles on XC-72 (C-AuPt), were also synthesized by the same procedure.

2.4. Materials characterization

The crystallinities of the catalysts were studied using a SEIFERT 2000 X-ray diffractometer equipped with a $\text{Cu K}\alpha$ radiation source



Scheme 1. Synthetic procedure of PVP-NGs-AuPt catalysts.

($\lambda = 0.1540 \text{ nm}$). The X-ray diffraction (XRD) patterns were identified by following the JCPDS files. The Scherrer and Bragg's formulae were used to calculate the mean diameter and the lattice parameters for each sample. Scanning electron microscopic (SEM) images were taken with a Zeiss Supra 40 FE SEM. TEM images were acquired with a HRTEM (2010F, JEOL model), which was operated at an accelerating voltage of 200 kV. Samples for TEM were prepared by suspending the catalysts on standard carbon-coated Cu grid. Energy-dispersive X-ray spectra (EDX) were obtained with a Link ISIS EDX detector coupled with the transmission electron microscope. The textural properties were analyzed by the BET method using a Quantachrome Autosorb instrument (Model AS1-CT) with nitrogen as the adsorbate [49]. The total volume (V_{tot}) and the micropore volumes (V_{m}) were derived from nitrogen sorption isotherm, and the pore size distribution was obtained according to Barrett–Joyner–Halenda (BJH) model. The X-ray photoelectron spectra (XPS) were taken using an Axis Ultra DLD X-ray photoelectron spectrometer equipped with an $\text{Al-K}\alpha$ radiation source of 150 W. The resolutions were 1 eV for XPS survey scans and 0.05 eV for the XPS fine scans. The CasaXPS software version 2.3.14 program was used to subtract the Shirley background, analyze the composition and deconvolute the XPS peaks. The survey and fine scan XPS spectra were calibrated with the $\text{sp}^2 \text{ C}1\text{s}$ band at 284.5 eV.

2.5. Electrode preparation and electrochemical studies

A catalyst ink was prepared by mixing the catalyst with 5 wt% Nafion ionomer in 2-propanol solution. It was then deposited onto the graphite block. The catalyst loading was kept at 0.40 mg cm^{-2} , and the geometrical surface area of the graphite block was 0.65 cm^2 . Electrochemical measurements were conducted in a three-electrode cell using a computer-controlled Autolab 302N potentiostat/galvanostat. Ag/AgCl , a Pt foil and a catalyst were used as the reference, counter and working electrodes, respectively. The electrolyte consisting of 1 M ethanol and 0.5 M NaOH were purged with XL grade N_2 before each experiment. An ion exchange chromatography (IC) system by Metrohm's Ltd coupled with an L-7100 pump and a conductivity detector was used to analyze the reaction products during EOR. The Metrosep A Supp 5-250 and Metrosep A Supp 4-550 columns were employed to quantify the yields of acetate and carbonate ions.

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