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Article

Composition-controlled synthesis of platinum and palladium nanoalloys as highly active electrocatalysts for methanol oxidation

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ABSTRACT

Platinum and palladium (PtPd) alloy nanoparticles (NPs) are excellent catalysts for direct methanol fuel cells. In this study, we developed PtPd alloy NPs through the co-reduction of K_2PtCl_4 and Na_2PdCl_4 in a polyol synthesis environment. During the reaction, the feed molar ratio of the two precursors was carried over to the final products, which have a narrow size distribution with a mean size of approximately 4 nm. The catalytic activity for methanol oxidation reactions possible depends closely on the composition of as-prepared PtPd alloy NPs, and the NPs with a Pt atomic percentage of approximately 75% result in higher activity and stability with a mass specific activity that is 7 times greater than that of commercial Pt/C catalysts. The results indicate that through composition control, PtPd alloy NPs can improve the effectiveness of catalytic performance.

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1. Introduction

Platinum nanoparticles (NPs) are key electrocatalysts that are used in industrial processes and commercial devices, particularly for direct methanol fuel cells (DMFCs), which are used as sustainable replacements for traditional fossil fuels [1–5]. DMFCs have unique physical and chemical properties as well as the ability to facilitate both oxidation and reduction reactions [6,7]. However, there are two major drawbacks of these catalysts: Pt is expensive and scarce, and Pt NPs are easily contaminated by the carbon monoxide (CO) that is generated as an intermediate species during methanol oxidation reactions (MORs) [8,9]. Therefore, it is necessary to improve catalytic performance while conserving Pt.

One way of overcoming these problems is to prepare Pt NPs with high active specific surface areas. By downsizing NPs, a high surface-to-volume ratio is achieved, thus, enhancing the rate of efficiency at which the catalysts utilize metals [10]. Also, adjusting specific facets, edges, corners, and defects of NPs so that they can provide more active reaction sites to optimize the catalytic properties [11,12]. Another major strategy for improving the catalytic activity of NPs is to combine Pt with another metallic element into bimetallic alloys. Recently, there have been reports on bimetallic Pt-M (M = Pd, Au, Ag, Ru, Fe, Co, Ni, etc.) catalysts with increased electrocatalytic activity that also minimize the consumption of Pt [14–20]. For example, the DMFC performance increased in the order of Pt/C < Pt-Fe/C < Pt-Co/C ≈ Pt-Cr/C [20].

Due to its proximity to Pt in the periodic table, Pd is considered a prime candidate for building platinum and palladium (PtPd) bimetallic catalysts, which are less expensive than pure Pt catalysts and exhibit excellent catalytic performance [21,22].

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Recent studies have indicated that PtPd alloy NPs may be useful as catalysts for the hydrogenation of aromatic hydrocarbons and for the electro-oxidation of small organic molecules (methanol, ethanol, etc.) with high sulfur [23] and CO tolerance [24] due to the bifunctional effect of NPs. In addition, the use of Pd instead of other metals such as Cu, Ag, Co, or Ni could also help minimize corrosion and loss of catalysts when said catalysts are used in an acidic environment such as proton-exchange membrane (PEM) fuel cells [25].

Over the past decade, many Pt-Pd bimetallic NPs with a rich variety of structures and shapes, such as core-shell structures, nanocages, and tetrahedra have been prepared [26–28]. Many methods for preparing bimetallic NPs have been developed, such as: co-chemical reduction, seed-mediated growth, electrochemical deposition, and galvanic replacement [29–32]. However, PtPd NPs synthesized from these methods lack either size or composition tunability over a wide range and are generally not suitable for composition-dependent catalytic studies.

In this study, ultrasmall PtPd alloy NPs with controls on sizes (4.0–7.0 nm) and compositions were developed. Monodisperse PtPd NPs were prepared via the co-reduction of K_2PtCl_4 and Na_2PdCl_4 with Poly (vinyl pyrrolidone) (PVP) in ethylene glycol (EG) solution. The PtPd NPs were active catalysts for MORs in an H_2SO_4 solution, and their activity was composition dependent. The PtPd alloy NPs with atomic Pt in 75% showed higher activity and durability than commercial Pt/C catalyst, and its mass specific activity was 7 times greater than that of commercial Pt/C catalysts. This study indicate that through the composition control, these PtPd alloy NPs can serve as an excellent platform for studying catalysis optimization.

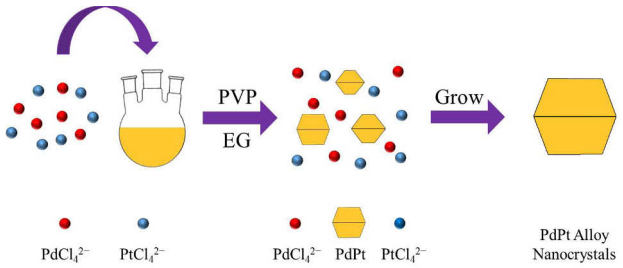
2. Experimental

2.1. Chemicals

Potassium tetrachloroplatinate (II) (K_2PtCl_4, AR), sodium tetrachloropalladate (Na_2PdCl_4, AR), ethylene glycol (EG, AR), and acetone and poly (vinyl pyrrolidone) (PVP, M_w = 55,000) were purchased from Aladdin (Shanghai, China). Vulcan XC-72R was received from Cabot (Boston, MA, USA) and 5% Nafion was purchased from Sigma (Shanghai, China). All reagents were used without further purification. High-purity deionized water (>18.4 MΩ·cm) was produced using Millipore A10 Milli-Q (Darmstadt, Germany).

2.2. Synthesis of PtPd NPs

PtPd alloy NPs were synthesized using a polyol method, in which Na_2PdCl_4 and K_2PtCl_4 served as the metal precursors, while PVP and EG served as a stabilizer and strong reductant, respectively. PVP was also used as a weak reductant due to its hydroxy (OH) end groups [33]. The process of synthesizing uniform PtPd alloy NPs is shown in Scheme 1. PVP (105 mg) was dissolved in EG (8 mL) and heated to 110 °C in air under magnetic stirring. Meanwhile, Na_2PdCl_4 (28.5 mg, 0.1 mmol) and K_2PtCl_4 (40.4 mg, 0.1 mmol) were co-dissolved in EG (3 mL) at room temperature. The EG solution of K_2PtCl_4 and



Scheme 1. Illustration of the synthetic pathway leading to the formation of PtPd alloy nanoparticles.

Na_2PdCl_4 was then added dropwise to the PVP solution. The reaction mixture was heated at 110 °C in air for 5 h. After the mixture had cooled to room temperature, the PtPd NPs were centrifuged (13500 r/min, 30 min) and washed three times with acetone to remove excess PVP and EG. The products were dispersed and preserved in ethanol. Finally, the as-prepared solution of PtPd NPs was dried in a vacuum oven at 70 °C for 8 h. The Pt/Pd atomic ratio was controlled by the Pt and Pd precursor ratios. The Pt1Pd3, Pt1Pd1 and Pt3Pd1 NPs were synthesized by using K_2PtCl_4 and Na_2PdCl_4 of 0.3 mmol/0.1 mmol, 0.1 mmol/0.1mmol, and 0.1mmol/0.3 mmol, respectively.

2.3. Synthesis of PtPd/Vulcan XC-72R

Two milligrams of PtPd NPs in acetone were mixed with 10 mg of carbon black (Vulcan XC-72R) and sonicated for 1 h to load all the NPs on carbon black. The PtPd/Vulcan XC-72R was separated by centrifugation (13500 r/min, 10 min) and further purified twice by deionized water and dried in a vacuum oven at 70 °C for 8 h. Finally, the PtPd/C was suspended in ethanol by sonication to form a PtPd/ Vulcan XC-72R suspension (2 mg/mL). The commercial Pt/C (E-TEK, 30% Pt loading) was used without any treatment and was sonicated with ethanol to form a commercial Pt/C catalyst suspension (2 mg/mL).

2.4. Electrocatalytic evaluation

All the electrochemical characterizations were carried out using a workstation (CHI660D, Chen Hua, Shanghai, China) and a three-electrode configuration with a glassy carbon (GC) electrode, a saturated calomel electrode (SCE), and a platinum foil as the working electrode, reference electrode and counter electrode, respectively. Prior to use, the GCE was carefully polished with alumina paste for 30 s, thoroughly cleaned, and air-dried. For cyclic voltammogram (CV) measurements, 20 μL of a catalyst dispersion was dropped onto the GC electrode and dried at room temperature. After solvent evaporation, 10 μL of 0.05 wt% Nafion solution were dropped onto the surface of the GCE and air-dried. Cyclic voltammetry was first conducted at 50 mV/s in 0.5 mol/L H_2SO_4 solution within the potential range −0.25 to 1.0 V (vs SCE). Before data collection, each catalyst modified electrode was cleaned and activated in the electrolyte solution for several cycles to ensure that a stable CV was obtained. The CVs were used to estimate the electrochemical active surface area (ECASA) of the catalyst by calculating the hy-

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