



# Gold-decorated platinum nanoparticles in polyelectrolyte multilayers with enhanced catalytic activity for methanol oxidation

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## ABSTRACT

In the development of commercial direct methanol fuel cells, search for alternative electrocatalysts for Pt with superior catalytic activity and long-term operation stability remains a major challenge. This paper reports the synthesis of Au-decorated-Pt (Pt<sup>+</sup>Au) nanoparticles in polyelectrolyte multilayers (PEMUs) via ion-exchange/in situ reduction cycles in conjunction with a seed-mediated growth process. The structure of the Pt<sup>+</sup>Au nanoparticles in the PEMU was characterized by UV–vis absorption spectroscopy, transmission electron microscopy and selected-area electron diffraction. The electrocatalytic performance of the nanoparticles for methanol oxidation reaction was investigated by cyclic voltammetry, and the results show that the Pt<sup>+</sup>Au nanoparticles exhibited better electrocatalytic efficiency, tolerance to poisoning and long-term stability compared with monometallic Pt, showing synergistic effects between the bimetallic components. The PEMU-supported Pt<sup>+</sup>Au nanoparticles may find application as an anode catalyst in direct methanol fuel cells.

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## 1. Introduction

Direct methanol fuel cells (DMFCs) have received a great deal of interest due to their potential as power sources for portable devices, including mobile phones, personal digital assistants, laptop computers, or even for electric vehicles [1]. DMFCs offer several key advantages, such as high energy density, high efficiency of fuel utilization, low operating temperature and low emission of pollutants, and operate without the need of a hydrogen reformer and the hydrogen storage issue in comparison with hydrogen fuel cells [2,3].

One major challenge in the development of commercial DMFCs is the poor performance and high cost of the anode catalysts [2–4]. The traditional Pt catalyst exhibits sluggish electrooxidation because of poisoning by CO-like intermediate species, resulting in decreased electrochemically active surface area [2–5]. To address this problem, one of the most successful strategies is to use oxophilic metals to form binary, ternary and even quaternary Pt-based alloys to improve CO tolerance of the catalyst [6–8]. Current state-of-the-art catalysts rely almost exclusively on Pt–Ru alloy nanoparticles dispersed onto a carbon support. Unfortunately, Ru tends to dissolve in the acidic electrolyte, contaminating the

cathode catalyst, and degrading the long-term performance of the DMFCs [9,10]. In contrast, Au is inert to acids [11], and recently, Au-containing catalysts, such as Au/Pt nanosponges [12] and dendritic Au@Pt core-shell nanoparticles [13], were found to show excellent electrocatalytic activities for methanol oxidation at low temperatures. In heterogeneous catalysis, smaller nanoparticles provide larger active surface areas, but smaller nanoparticles are less stable and can easily aggregate, leading to poor long-term performance. Therefore the nanoparticles are often immobilized on a support, such as carbon materials [5,7,10,14]. However, it has been reported that metal particles smaller than 2 nm are readily pocketed by the micropores of the conductive carbon supporting materials, making them unavailable in the electrochemical reactions, which leads to a significant decrease in the overall Pt utilization [14,15]. Moreover, the strong interactions between the catalyst particles and the surface of the supporting materials can reduce their catalytic activity for DMFCs [16–18]. Therefore, the search for an electrocatalyst for DMFCs with superior catalytic activity and long-term operation stability remains an important issue to be addressed.

The layer-by-layer (LbL) self-assembly technique is a facile, versatile, and inexpensive approach to functional thin films that allows a wide variety of species to be incorporated within the film structure [19–21]. This technique has found application in numerous fields including antireflection coatings [22], antibacterial coatings [23–25], superhydrophobic surfaces [26], surface-enhanced Raman spectroscopy [27,28] and catalysis [29,30]. In fuel cells LbL films

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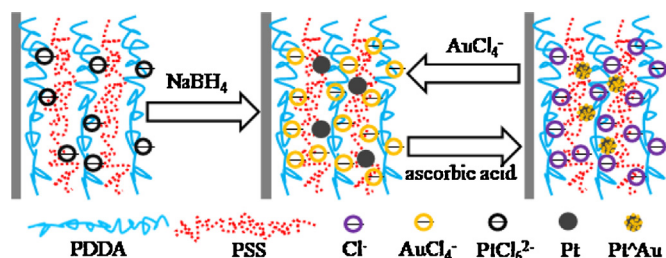


Fig. 1. Schematic illustration of the synthesis of Pt<sup>+</sup>Au nanoparticles.

have been employed as proton exchange membranes due to ease of fabrication, precise control and tunability of the film properties [31], and as support material for fuel cell catalyst due to their intimate contact with catalyst particles, resistance to fuel permeation and stabilization of the catalyst particles [21,32–34]. In the present study, we report facile synthesis of Pt nanoparticles decorated with Au (Pt<sup>+</sup>Au, Fig. 1) in situ in PEMUs, which serve as both nanoreactors and supports for the nanoparticles. The Pt<sup>+</sup>Au nanoparticles were characterized by UV–vis spectroscopy, transmission electron microscopy (TEM) and selected-area electron diffraction (SAED), and their electrocatalytic activity and long-term stability for methanol oxidation was investigated by cyclic voltammetry (CV). The results demonstrate that the PEMU-supported Pt<sup>+</sup>Au nanoparticles are superior to Pt catalyst for methanol oxidation.

## 2. Experimental

### 2.1. Materials

Hexachloroplatinum (IV) acid hydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) was purchased from Shanghai First Reagent Factory. Chloroauric acid tetrahydrate ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ) was obtained from Sinopharm Chemical Reagent Co., Ltd. Ascorbic acid (AA) was provided by Huishi Biochemical Co., Ltd., (Shanghai, China). Sodium chloride (NaCl), sodium hydroxide (NaOH), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and methanol, all of analytical grade, were supplied by Beijing Chemical Reagents Company. Poly(diallyldimethylammonium chloride) (PDPA, 20 wt% in water,  $M_w \approx 200\text{--}350\text{ k}$ ), poly(styrene sulfonate) (PSS,  $M_w \approx 70\text{ k}$ ) and sodium borohydride ( $\text{NaBH}_4$ ) were purchased from Aldrich. All chemicals were used as received without further purification. Ultrapure water (Millipore Milli-Q,  $18.2\text{ M}\Omega\text{ cm}$  at  $25^\circ\text{C}$ ) was used in all experiments.

### 2.2. Substrate treatment

Quartz slides used for UV–vis analysis and glass slides used for other tests were cleaned in a boiling piranha solution (98%  $\text{H}_2\text{SO}_4$ :30%  $\text{H}_2\text{O}_2$ , 70:30 v/v) at  $80^\circ\text{C}$  for 1 h and then washed by copious amounts of water. FTO conducting glass slides (Nippon Sheet Glass, Solar, 2.2 mm thick) with  $1.0\text{ cm} \times 3.3\text{ cm}$  dimensions were ultrasonicated in each of the following solvents, soap water, water, chloroform, acetone, and 1 M NaOH aqueous solution, for 15 min and then rinsed thoroughly with water.

### 2.3. Preparation of (PDPA/PSS)<sub>4,5</sub> films

PEMUs were assembled following a previously reported procedure [21]. Freshly cleaned quartz, glass, and FTO slides were sequentially immersed into PDPA (1.0 mg/mL) and PSS (1.0 mg/mL) aqueous solutions containing 1.5 M NaCl for 30 min each with suf-

ficient water rinse in between until 4.5 bilayers were deposited, producing PEMUs capped by PDPA.

### 2.4. Synthesis of Au-decorated Pt nanoparticles in the PEMU

A (PDPA/PSS)<sub>4,5</sub> film was dipped into a  $\text{H}_2\text{PtCl}_6$  solution (1 mM) for 5 min, removed and rinsed with water, and then treated with a freshly prepared aqueous solution of  $\text{NaBH}_4$  (0.1 M) for 5 min. This ion-exchange/reduction cycle was repeated  $m$  times to yield Pt nanoparticles ( $\text{Pt}_m$ ) embedded in the PEMU. Then, the PEMU loaded with  $\text{Pt}_m$  nanoparticles was immersed in  $\text{HAuCl}_4$  (0.1 mM) and ascorbic acid (0.1 M) solutions, respectively, for 5 min each with sufficient water rinse in between, and the process was repeated  $n$  times to produce a PEMU containing Pt nanoparticles decorated with Au, denoted  $\text{Pt}_m\text{-Au}_n$ , where  $m$  and  $n$  represents the corresponding ion-exchange/reduction cycle number for Pt and Au, respectively. Finally, the PEMU carrying the  $\text{Pt}_{10}\text{-Au}_n$  particles was rinsed thoroughly with  $\text{H}_2\text{SO}_4$  (1 M) to avoid chloride poisoning.

### 2.5. Characterization

UV–vis spectra of the PEMUs loaded with nanoparticles were collected on a TU1901 spectrometer (Beijing Purkinje General Instrument Co., Ltd.) at room temperature. TEM micrographs and corresponding SAED patterns of the metal nanoparticles were acquired on a JEOL1011 microscope operating at a 100 kV accelerating voltage. A small piece of the PEMU film loaded with metal nanoparticles was peeled off from the substrate using dilute hydrofluoric acid, floated in water, and then transferred to a carbon-coated copper grid for the characterization.

### 2.6. Electrochemical studies

Catalytic properties of the PEMU-supported nanoparticles were evaluated by CV at room temperature in a homemade airtight three-electrode cell containing 1 M methanol and 0.5 M  $\text{H}_2\text{SO}_4$ . Details of the homemade cell were described in a previous report [21]. The FTO electrode coated with the PEMU containing nanoparticles served as the working electrode. A Pt wire was used as the auxiliary electrode, and a Ag/AgCl (saturated by KCl solution) electrode was placed in the cell near the working electrode. Cyclic potential was swept in a potential range of 0–1.0 V (vs the Ag/AgCl reference electrode) at a rate of 50 mV/s. Prior to performing the CV measurements, the electrolyte was purged with  $\text{N}_2$  gas for 30 min to remove  $\text{O}_2$ . The electrochemically active surface (EAS) area of all samples was estimated by the region of hydrogen desorption in a deoxygenated 0.5 M  $\text{H}_2\text{SO}_4$  aqueous solution at a sweeping rate of 50 mV/s. All data presented were collected from stable voltammetry curves except for the electrochemical activity and stability studies.

## 3. Results and discussion

In the synthesis of the Pt–Au bimetallic nanoparticles in the PEMU, the first stage, formation of the Pt nanoparticles, was accomplished using a strong reducing agent,  $\text{NaBH}_4$ , and in the second stage the  $\text{AuCl}_4^-$  ions were reduced using ascorbic acid, a weak reducing agent, so that the Au reduced only grew on the existing nuclei, acted by the Pt nanoparticles. Fig. 2 displays the UV–vis spectrum for Au nanoparticles produced in the PEMU via direct reduction of the  $\text{AuCl}_4^-$  ions by ascorbic acid, which exhibits a very broad surface plasma resonance (SPR) peak centered at  $\sim 750\text{ nm}$ , suggesting much larger (and fewer) nanoparticles than that produced by  $\text{NaBH}_4$ , which display an SPR peak typically at  $\sim 530\text{ nm}$  [13,27,30,35]. Most likely the quartz substrate provided the scarce

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