



# Platinum nanoparticles on carbon-nanotube support prepared by room-temperature reduction with H<sub>2</sub> in ethylene glycol/water mixed solvent as catalysts for polymer electrolyte membrane fuel cells



Yuying Zheng<sup>a</sup>, Zhengjie Dou<sup>a</sup>, Yanxiong Fang<sup>a</sup>, Muwu Li<sup>b</sup>, Xin Wu<sup>b</sup>, Jianhuang Zeng<sup>b,\*</sup>, Zhaohui Hou<sup>c</sup>, Shijun Liao<sup>b</sup>

<sup>a</sup> School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China

<sup>b</sup> School of Chemistry and Chemical Engineering, South China University of Technology, Guangdong Key Lab for Fuel Cell Technology, Guangzhou 510641, China

<sup>c</sup> Department of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang 414000, China

## HIGHLIGHTS

- H<sub>2</sub> reduction of Pt(IV) in EG/water solvent was used to produce Pt nanoparticles.
- EG/water = 1:1 is the optimal volume ratio to synthesize 3 nm Pt nanoparticles.
- Pt(50)/CNT exhibited excellent methanol oxidation and oxygen reduction activities.

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## ABSTRACT

Polyol approach is commonly used in synthesizing Pt nanoparticles in polymer electrolyte membrane fuel cells. However, the application of this process consumes a great deal of time and energy, as the reduction of precursors requires elevated temperatures and several hours. Moreover, the ethylene glycol and its oxidizing products bound to Pt are difficult to remove. In this work, we utilize the advantages of ethylene glycol and prepare Pt nanoparticles through a room-temperature hydrogen gas reduction in an ethylene glycol/water mixed solvent, which is followed by subsequent harvesting by carbon nanotubes as electrocatalysts. This method is simple, facile, and time-efficient, as the entire room-temperature reduction process is completed in a few minutes. As the solvent changes from water to an ethylene glycol/water mix, the size of Pt nanoparticles varies from 10 to 3 nm and their shape transitions from polyhedral to spherical. Pt nanoparticles prepared in a 1:1 volume ratio mixture of ethylene glycol/water are uniformly dispersed with an average size of ~3 nm. The optimized carbon nanotube-supported Pt electrocatalyst exhibits excellent methanol oxidation and oxygen reduction activities. This work demonstrates the potential use of mixed solvents as an approach in materials synthesis.

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## 1. Introduction

Although researchers have spent decades to investigate polymer electrolyte membrane fuel cells (PEMFCs), their commercialization is still hampered by several obstacles, such as the lack of a way to develop electrocatalysts in a simple, facile, and cost-effective manner [1–3]. Pt nanoparticles are considered standard

electrocatalysts because they are highly active in the catalytic oxidation of hydrogen and small organic molecules, such as methanol, ethanol, and formic acid in PEMFCs [4–6]. Pt nanoparticles are typically dispersed on different types of carbon supports to achieve high dispersion and maximize the utilization of noble metals [7]. Because of high over-potentials at the electrodes during repeated start-up/shut-down, fuel starvation, and other harsh operational conditions, conventionally used carbon black supports are prone to corrosion, which leads to Pt dissolution and deactivation [8,9]. Graphitized carbons, such as carbon nanotubes (CNTs), were found to be good substitutes because they possess

\* Corresponding author.

E-mail address: [cejhzeng@scut.edu.cn](mailto:cejhzeng@scut.edu.cn) (J. Zeng).

higher corrosion resistance than carbon black [10].

The synthesis of sub-nanosized uniform Pt nanoparticles in PEMFCs is of great interest. Numerous preparation methods have been reported for such purpose [11–17]. Among these methods, polyol reduction is considered the most classical [18–22]. In a representative polyol method, ethylene glycol (EG) is heated at elevated temperatures in a conventional oil bath, a microwave, or an autoclave (hydrothermal reaction), in which EG acts as a reducing and protecting agent. Although this method can easily produce 3–5 nm Pt nanoparticles with uniform distribution, it is hindered by a number of limitations. Heating at high temperatures and using pure EG as a reactant require excessive washing of the Pt nanoparticles with water, thereby showing that this process is energy-consuming and not environment-friendly. Most importantly, the products of EG oxidation (i.e., aldehydes or carboxylic acids), which are strongly bound to Pt, are difficult to remove by rinsing, leading to the loss of clean Pt active sites [23,24]. Room-temperature hydrogen gas reduction is a conventional yet simple method for producing Pt and Pd nanoparticles [25,26]. The reduction process was completed by bubbling hydrogen gas in an aqueous solution containing noble metal precursors. We modified this method by quickly injecting Pt precursor solutions into an aqueous solution saturated with hydrogen gas to synthesize polyhedral Pt nanoparticles with high catalytic activity for methanol electrooxidation [15]. Although capable of producing active polyhedral Pt, this method was time-consuming (lasting from a few hours to a couple of days), and the prepared Pt nanoparticles were large (~10 nm) [15,25]. We recently reconsidered this method and prepared ~3.8 nm Pd/C catalysts through the hydrogen gas reduction of Pd(II) precursor in pure EG for formic acid oxidation. Instead of using pure water as the conventional solvent, pure EG with high viscosity was used to hamper Pd particle aggregation during formation. Nonetheless, EG rendered a good protecting effect [27]. Solvents used in the synthesis play a critical role in controlling the morphology and sizes of resulting nanoparticles [28–30]. In the present work, we combined the benefits of water and EG, and investigated the effects of mixed solvent on the preparation of Pt nanoparticles by hydrogen gas reduction at room temperature. The simple and facile reduction of Pt precursors was completed in a few minutes at room temperature in an EG/water mixed solvent. In addition, the amount of EG used in the synthesis was substantially reduced, leading to less EG disposal and easier cleaning of Pt nanoparticles at the subsequent stage. This process completely differs from the conventional polyol process, because EG was non-reactive and used as a solvent only, and no obstinate aldehydes or carboxylic acids were produced. Pt nanoparticles with an average particle size of 3 nm prepared in 50:50 (v:v) EG/water mixed solvent were supported on CNTs and tested for methanol oxidation and oxygen reduction reaction (ORR) with satisfactory performances.

## 2. Experimental section

### 2.1. Electrocatalyst preparation

Sodium citrate ( $\text{Na}_3\text{Cit}$ ) and hexachloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) were dissolved either in EG or water to produce 0.038 M solutions ( $\text{Cit}^{3-}/\text{EG}$  and  $\text{Cit}^{3-}/\text{H}_2\text{O}$ ,  $\text{Pt}^{4+}/\text{EG}$ , and  $\text{Pt}^{4+}/\text{H}_2\text{O}$ ). In a typical experiment, 11 ml of EG and 7 ml of water were mixed together. Then, 4.1 ml of  $\text{Pt}^{4+}/\text{EG}$  and 8.2 ml of  $\text{Cit}^{3-}/\text{H}_2\text{O}$  were added into a 50 ml ground-glass stoppered bottle (volume ratio of EG to water in the reaction mixture was 50:50). The pH of the solution was left unadjusted. Pt(IV) reduction was completed by bubbling hydrogen gas for a few minutes into the mixture under magnetic stirring. The color of the solution changed from pale yellow to gray, indicating

the formation of Pt nanoparticles. Finally, 120 mg of acid-treated CNTs (Chengdu Organic Co. Ltd., Chinese Academy of Sciences, China) were added to harvest the freshly prepared Pt nanoparticles. The ink suspension was filtered by using a polytetrafluoroethylene filter to recover the solid product, which was copiously washed with hot deionized water (~50 °C) before being dried in vacuum at 70 °C overnight. The molar ratio of sodium citrate to hexachloroplatinic acid was maintained at 2:1, as this ratio resulted in satisfactory protection with minimal negative effects [27]. The amount of added CNT was pre-calculated to obtain 150 mg of electrocatalyst with a Pt loading of 20 wt.%. The electrocatalyst obtained was denoted as Pt(50)/CNT, where 50 indicated the EG volume. Similarly, Pt(0)/CNT, Pt(10)/CNT, and Pt(100)/CNT were prepared with the use of pure water, 10:90 EG/water mixed solvent, and pure EG, respectively.

### 2.2. Material and electrochemical characterizations

Transmission electron microscopy (TEM) was made using an FEI Tecnai G2 F20 S-Twin with an accelerating voltage of 200 kV to obtain particle size, shape, and size distribution. X-ray powder diffraction patterns of the electrocatalysts were recorded by a Rigaku D/Max-3B diffractometer (Shimadzu), using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The  $2\theta$  angles were scanned from 20° to 80° at a rate of  $2^\circ \text{ min}^{-1}$ . Thermogravimetric analysis was performed on a Thermal Analysis Instruments Q600 SDT (TA, USA) in  $100 \text{ ml min}^{-1}$  under continuous air flow and with a ramp of  $10^\circ \text{ C min}^{-1}$ . A conventional three-compartment electrochemical cell was used to evaluate the electrocatalysts. An Autolab PGSTAT302N served as the potentiostat/galvanostat. A rotating disk electrode (RDE, Pine Instrument Company, Model AFMSRCE) was used as the working electrode. The electrocatalyst layer on the RDE was fabricated by casting 5  $\mu\text{l}$  of catalyst ink by micropipette (ink formation: 5 mg of electrocatalysts + 1 ml of 0.25 wt % Nafion® 117 diluted with ethanol) onto a 5 mm diameter vitreous glassy carbon disk electrode. The Pt loading on the working electrode was then calculated to be  $5 \mu\text{g}$  or  $25.5 \mu\text{g cm}^{-2}$ . A Pt wire and an Ag/AgCl electrode in 3 M KCl were used as the counter and reference electrodes, respectively, and 0.5 M methanol in 0.5 M  $\text{H}_2\text{SO}_4$  served as the electrolyte for methanol oxidation. The electrochemical surface area was evaluated by CO stripping; 10% CO in Ar gas was employed. The 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte was saturated with gas while the electrode was held at  $-0.1 \text{ V}$  for 30 min. After CO adsorption, the bulk CO was removed, and the electrolyte was thoroughly purged by high-purity Ar. Catalytic activity toward ORR was measured in 0.5 M  $\text{H}_2\text{SO}_4$  when the electrolyte was saturated with pure oxygen, and the working electrode was rotated at 1600 rpm. All reported potentials were referenced to Ag/AgCl in 3 M KCl, and electrochemical tests were recorded at room temperature.

## 3. Results and discussion

Inherently, platinum nanoparticles with high surface areas are thermodynamically unstable versus agglomeration to the bulk. Manipulating reaction solvents is a good approach for modifying particle size and morphology [29,31,32]. When hydrogen gas was bubbled into the solution containing Pt precursors, Pt nuclei were formed, and the hindrance toward agglomeration was caused by the surrounding solvent molecules and protecting agents. Solution viscosity and density are two factors that regulate mobility and are therefore responsible for manipulating the size and dispersion of the particles. The physical properties (i.e., viscosity and density) of EG/water mixed solvents at 25 °C are presented in Fig. 1 (the data were selected from Ref. [33] and re-plotted for clarity). Although

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