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An acetic acid refluxing-electrochemistry combined strategy to activate supported-platinum electrocatalysts

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ABSTRACT

Surfactant removal from the surface of platinum-based nanoparticles prepared using solution-based methods is a prerequisite to realize their high catalytic performance for electrochemical reactions. Herein, we report an effective approach combining acetic acid refluxing with an electrochemical process for the removal of amine- or thiol-based capping agents from the surface of supported-platinum nanoparticles. This strategy involves surfactant protonation by refluxing the supported-platinum particles in acetic acid followed by surfactant removal by subsequent electrochemical treatment at high potential. We demonstrate that this combined activation process is essential to enhance platinum particle performance in catalyzing direct methanol fuel cell reactions, including methanol oxidation and oxygen reduction reactions. The studies in this work show promise in electrocatalysis applications of solution-based materials synthesis.

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Introduction

Recently there have been great advances in platinum (Pt)-based electrocatalysts produced by solution-based methods (Chen, Lim, Lee, & Xia, 2009; Peng & Yang, 2009; Xia, Xiong, Lim, & Skrabalak, 2009; Chen & Holt-Hindle, 2010; Yang, 2011; Liu et al., 2015; Qu et al., 2016). In a solution-based synthetic system, nanoparticle nucleation and growth are easily controlled by reaction parameter design, to include: reactant concentration, the precursor/surfactant mole ratio, and reaction temperature and time. However, for solution-based Pt-based electrocatalysts, the surfactants ranging from small molecules to macromolecular reagents, which are typically employed to enhance nanoparticle stability in solution, would result in poor electrocatalytic performance of the Pt by occupying a large number of surface Pt atoms. Surface coverage results through the formation of strong, or even irreversible, interactions, typically coordinate (covalent) bonds (Karthikeyan, Giridhar, & Vasudevan,

2010; Yan, Yuan, & Dyson, 2013). For this reason, surfactants are often used as a protective agent to form stable nanoparticles, which are subsequently destroyed by annealing the catalysts at high temperatures; and preparation of electrodes requires a second ethanol treatment (Liu, Lee, Han, Chen, & Gan, 2002; Solla-Gullón, Vidal-Iglesias, Montiel, & Aldaz, 2004; Eklund & Cliffl, 2004; Xiong & Manthiram, 2005; Rojas et al., 2005; Li & Hsing, 2006; Sen & Cökaçaç, 2007). However, subjecting the samples to heat treatment inevitably results in changes in the properties of the core metal, including composition, morphology, and structure. A further concern by the application of heat treatment is to induce particle aggregation. Therefore, developing soft methods for surfactant removal from the surface of Pt-based nanoparticles would be of significance to control the core metal properties, and by extension, control catalytic activity and durability for electrochemical reactions.

In this study, we report an effective approach based on the combination of acetic acid refluxing with an electrochemical process for the removal of amine- or thiol-based protective surfactants from the surface of Pt nanoparticles supported on carbon substrates. This strategy involves surfactant protonation by refluxing the supported-Pt particles in acetic acid followed by surfactant removal by subsequent electrochemical treatment at high

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potential. We demonstrate the effectiveness of this combined activation process for enhancing the activity of Pt particles in catalyzing direct methanol fuel cell (DMFC) reactions, including the methanol oxidation reaction (MOR) and the oxygen reduction reaction (ORR). Considering the widespread use of amine- or thiol-based surfactants in solution-based synthesis of nanomaterials (Yang, Lee, Deivaraj, & Too, 2003; Eklund & Cliffler, 2004; Wang, Hou, Kim, & Sun, 2007; Liu et al., 2007; Wang, Daimon, Onodera, Koda, & Sun, 2008; Xu, Shen, Hou, Gao, & Sun, 2009; Liu et al., 2012, 2014b; Yang et al., 2012; Liu et al., 2014a; Feng et al., 2014a; Feng et al., 2014b; Han et al., 2014), the studies in this work show promise as a strategy for synthesizing highly active catalysts for catalytic applications other than methanol oxidation and oxygen reduction.

Experimental

Chemicals

Platinum(II) acetylacetonate ($\text{Pt}(\text{acac})_2$, 97%), potassium tetrachloroplatinate(II) (K_2PtCl_4 , 98%), oleylamine (OLA, 70%, technical grade), dodecylamine (DDA, 98%), 1-dodecanethiol (DDT, 98%), acetic acid (CH_3COOH , 98%), sodium borohydride (NaBH_4 , 98%), trisodium citrate dihydrate ($\geq 99\%$), aqueous HClO_4 solution (70%, ACS reagent), and Nafion 117 solution (5% in a mixture of lower aliphatic alcohols and water) were purchased from Sigma–Aldrich (St. Louis, USA). Methanol (99%), ethanol (99.5%), and toluene (99.5%) were supplied by Beijing Chemical Works (Beijing, China), and Vulcan XC-72 carbon powders (XC-72C) possessing a BET surface area of ca. $250 \text{ m}^2/\text{g}$ and an average particle size of ca. 40–50 nm were purchased from Cabot (Boston, MA, USA). All materials were used as received. All glassware and Teflon-coated magnetic stirrer bars were cleaned with aqua regia, followed by copious rinsing with de-ionized water before drying in an oven.

Synthesis of OLA-stabilized Pt nanoparticles

In a typical synthesis of OLA-stabilized Pt nanoparticles (labeled as OLA-Pt), 0.4 mM of $\text{Pt}(\text{acac})_2$ was dissolved in 20 mL of OLA placed within a three-necked flask equipped with a condenser and stirrer bar. The solution was heated to 190°C under flowing N_2 and maintained at this condition for 2 h for the reduction of Pt^{2+} ions by OLA, which also served as the protective agent. After the reaction, the Pt nanoparticles were purified by precipitation with methanol, followed by centrifugation and methanol washing before re-dispersing in 20 mL of toluene.

Synthesis of DDA/DDT-stabilized Pt nanoparticles

The DDA/DDT-stabilized Pt nanoparticles were prepared using an ethanol-mediated phase transfer protocol (Yang et al., 2004;

Yang et al., 2009; Yang et al., 2011). First, the Pt nanoparticles were prepared in an aqueous phase by NaBH_4 reduction in the presence of sodium citrate. In a typical experiment, 6 mL of 100 mM aqueous sodium citrate solution was added to 150 mL of 1 mM aqueous K_2PtCl_4 solution. Thereafter, under vigorous stirring, 4.5 mL of 100 mM aqueous NaBH_4 solution was introduced dropwise to produce the Pt hydrosol, in which sodium citrate serves as the protective reagent. The molar ratio of NaBH_4 to the valence of Pt metal in their salts was maintained above 1.5 to ensure the reduction of the Pt ions to the zero valent state. After the reaction, the Pt hydrosol was aged overnight to decompose residual NaBH_4 .

Regarding the preparation of DDA- or DDT-stabilized Pt nanoparticles via the phase transfer method, a 50 mL aliquot of as-prepared Pt hydrosol was mixed with 50 mL of ethanol containing 1 mL of DDA or DDT, and the mixture was stirred for 2 min. Subsequently, a 50 mL aliquot of toluene was added, and stirring continued for an additional 3 min. The DDA- or DDT-stabilized Pt nanoparticles, labeled as DDA-Pt or DDT-Pt, were extracted into the toluene layer rapidly, leaving behind a colorless aqueous solution.

Pt nanoparticle loading on carbon substrates

For Pt nanoparticle loading on Vulcan XC-72 carbon substrates, a calculated amount of carbon powders was added to the toluene solution of OLA-, DDA-, or DDT-Pt nanoparticles. After stirring the mixture for 24 h, the carbon-supported Pt nanoparticles (20 wt% Pt on carbon substrates), labeled as OLA-Pt/C, DDA-Pt/C, or DDT-Pt/C, respectively, were collected by centrifugation, washed thrice with methanol, and thereafter dried at room temperature under vacuum for further experiments. Furthermore, the supernatants were retained to determine the loading efficiency of Pt particles from the colloidal solutions.

Protonating amine- or thiol-based surfactants

In a typical process, OLA-Pt/C, DDA-Pt/C, or DDT-Pt/C was mixed with 20 mL of acetic acid placed in a three-necked flask equipped with a condenser and stirrer bar and refluxed at 120°C for 3 h under flowing N_2 before obtaining the OLA-Pt/C, DDA-Pt/C, or DDT-Pt/C materials by centrifugation, followed by washing with de-ionized water, and drying at room temperature.

Particle characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed using a JEM-2100 (JEOL, Japan) electron microscope operating at 200 kV with the supplied software for automated electron tomography. For the TEM measurements, a drop of the nanoparticle solution was dispensed onto a 3 mm carbon-coated copper grid. Excessive solution was removed by

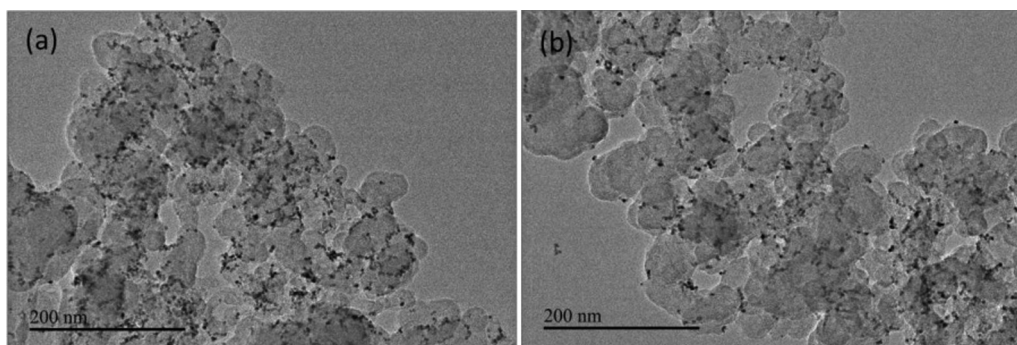


Fig. 1. Transmission electron microscopy images of carbon-supported Pt nanoparticles prepared by Pt loading from toluene (a) and the aqueous phase (b).

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