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Plasma-ionic liquid reduction for synthesizing platinum nanoparticles with size dependent crystallinity

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ABSTRACT

Platinum nanoparticles (PtNPs) were successfully synthesized using a liquid plasma system with 1-butyl-3-methylimidazolium tetrafluoroborate under atmospheric pressure. The PtNPs with a size of 3 nm were uniformly distributed on the surface of a copper grid. The particle size, shape and crystallinity of the Pt were further controlled by a mixture of hydrogen and argon gases, stabilizers and plasma reduction time. Furthermore, a smaller particle size had a better forward sweep of catalytic performance in oxidation of methanol while the cube-like structure was better for backward sweep of the electrochemical catalyst.

1. Introduction

Owing to their unique size-related structure and properties such as quantized electronic structure and high specific area, nanoparticles (NPs) have been attracting much attention as electrochemical catalysts as hydrogen oxidation, methanol oxidation, and oxygen reduction [1–4]. Both an active area and stability during operation are required for the material to be used as a catalyst [4]. Thus, Pt is traditionally the most popular material for electrochemical catalysts. So far, there have been numerous methods producing and utilizing PtNPs with high specific surface area [4–16]. Recent reports show that the catalytic activity of the metal depends on the particle size [17] and particle shape [18].

Until now, Pt has been mostly prepared from conventional methods based on colloidal techniques [5–19]. In such methods, PtNPs can be synthesized from the reduction of metal salt dissolved in a solution [6,7,19] or a hydrolysis/condensation route of forming the particles and their aggregates [10,11]. A stabilizer or stabilizing agents were also used in another route during the phase of particle formation [4]. There are, however, some drawbacks to the conventional methods: for example, long aging and reduction times, involvement of organic solvents in some processes, necessity of removing the stabilizers at the final stage, and preparation of complex molecular precursors [4]. Additionally, the use of chemical reducing agents, such as hydrogen gas, $LiBH_4$, $NaBH_4$, ethylene glycol, alcohol, etc. [4], can make additional disadvantages. Therefore, the development of a new method which overcomes the unfavorable process restrictions, such as organic solvents, stabilizing agents, long aging and reduction times and high chemical toxicity and so on, is still a challenge in the current development of catalysts.

Recently, microwave irradiation and plasma have been used to synthesize PtNPs with a short reduction time [4,20–27]. However, the stabilizers or hydrogen have still been used to control at the particle size of the PtNPs [4,20–27]. In addition, the complex systems are necessary to use a Pt electrode in liquid solution [4,20–25]. Very recently, we reported a new strategy to chemically bond PtNPs on multi-walled carbon nanotubes (MWNTs) in room temperature ionic liquid (RTIL) under atmospheric pressure plasma and to physically stabilize them through the film of ionic liquid supramolecules (ILSMs) on the surface of the PtNPs/MWNT [28]. The developed technology is able to overcome all the disadvantages.

Here, we report a systematic synthesis of PtNPs through a simple strategy of reducing Pt ions via ionic liquid-plasma reduction and also illustrate how effectively this process can control particle size and achieve narrow size distribution. We further electrochemically investigate the influence of particle size on the oxidation of methanol.

2. Experimental section

2.1. Materials

Chloroplatinic acid hydrate ($H_2PtCl_6.xH_2O$, 99.9% trace metals basis), 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMI]BF_4$),

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sodium dodecyl sulfonate (SDS), acetone and ethanol were purchased from Sigma-Aldrich, USA. Pristine MWNTs were purchased from Hanwha NanoTech, Korea. Argon and hydrogen gases were purchased from Yonhap L.P.G, Korea. Fiber polishing films with grit sizes of 6 and 3 μm were bought from Thorlabs Inc, USA. Nafion D521 solution (5 wt.%) was obtained from Dupont, USA. The electrolyte used was a mixture of 1 M methanol (Sigma-Aldrich) and 0.5 M sulfuric acid (Sigma-Aldrich) in distilled water.

2.2. *Synthesis of platinum nanoparticles*

A Pt precursor solution containing 20 mg precursor salt ($H_2PtCl_6.xH_2O$) in 5 g of ionic liquid was prepared first using a Branson Sonifier (Hwashin Technology Co. Ltd, Korea) for 15 min. Then, the mixture of the Pt precursor solution in the reactor, which had the structure shown in a previous study [28], was treated by an atmospheric pressure plasma system [29] (Ar, 200 W, 5 lpm) for 10 min. The gap between the power electrode and the reactor was 2 mm [28]. To control the size of the particles, 20 mg of SDS was added to the Pt precursor solution. To understand the forming of the NPs and controlling the number density of the NPs, a mixture of hydrogen and argon gases was used with a ratio of 10 sccm-H_2/5 lpm-Ar. After plasma reduction, the excess impurities were extracted from the ionic liquid by centrifuging it at 10,000 rpm for 10 min and repeating this procedure several times. After that, PtNPs were dispersed in 3 ml of ethanol and further analyzed.

2.3. *Characterization of Platinum nanoparticles*

The characterization of the synthesized PtNPs was performed using a transmission electron microscopy and energy-dispersive X-ray spectrometer (JEM-2100F, Joel, Japan). The weight percentage of the ILSM bound to the PtNPs surface and complexed with Pt was determined using thermal gravimetric analysis (TGA) (Mettler-Toledo Inc.) at a heating rate of 10 °C min^{-1} in an N_2 atmosphere. The chemical state of the PtNPs was analyzed by X-ray photoelectron spectroscopy (XPS) using a Sigma Probe Thermo Fisher VG Scientific spectrometer equipped with a monochromatic Al Kα X-ray source. The structure of the PtNPs was analyzed by X-ray diffraction (XRD) spectroscopy (Rigaku D/MAX-RC). The temporal evolution of the ionic liquid during plasma treatment was obtained by thermo hygrometer.

2.4. *Preparation of working electrode*

First, the glassy carbon plates were sequentially polished with fiber polishing films with different grit sizes of 6 and 3 μm. After that, they were washed by ethanol and dried in air. 1 mg of the PtNPs or PtNP/MWNT nanohybrids was dispersed in a mixture of 1 ml of ethanol and 50 μl of Nafion D521 solution using an ultrasonic for 30 min. Subsequently, 100 μl of the slurry was coated on the glassy carbon plate (1×1 cm^2) by drop-casting and then dried at 60 °C for 30 min to obtain the PtNPs/glassy carbon electrodes. Based on the geometric area, the surface density of PtNPs formed on the glassy carbon plate was 95 $\mu g cm^{-2}$.

2.5. *Measurement of methanol oxidation reaction*

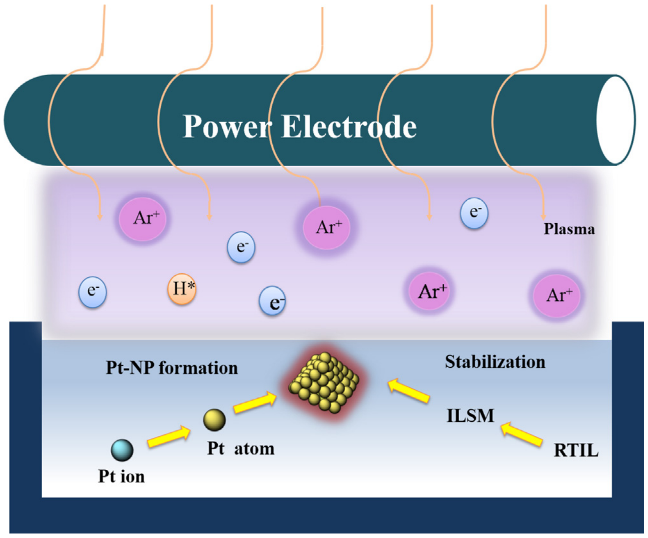
The characteristics of cyclic voltammograms (CVs) were assessed with an IviumStat device. Three electrode electrochemical cells were used. Pt and Hg/Hg^{2+} electrodes served as the CE and the reference electrodes, respectively. The activity for the methanol oxidation reaction was tested in a 0.5 M H_2SO_4 + 1 M CH_3OH solution. The CVs were recorded in a range of 1.2 to 0.0 V at a scan rate of 20 mVs^{-1}.

3. Results and Discussion

3.1. *Synthesis and characterization of PtNPs*

The synthesis of the PtNPs was achieved by using a plasma-RTIL system, as shown in Scheme 1. The color change of the solution phase from yellow to dark brown after plasma treatment, which demonstrates the synthesis of a large amount of PtNPs [30], the dissociation of an RTIL monomer and the formation of ILSMs due to the recombination of the radicals, also occurred under the high energy plasma flame [28,31] (see Supporting Information, Fig. S1). PtNPs were formed through the atomization reaction of the Pt precursor at the interface between the plasmas and RTIL due to hydrogen radicals and electrons as reducing agents [28]. The generation of reducing agents were described elsewhere [21–23,28,30–32]. Furthermore, the complex $[BMI]_2PtCl_4$ can be formed from the Pt compound and $[BMI]BF_4$ at around 70 °C due to the interaction between the chloride ions and hydrogen of the RTIL [28,33,34]. The change of the temperature of the ionic liquid solution during the plasma treatment is presented in Fig. S2 (Supporting Information). The temperature was leveled off at around 65 °C after 100 sec of plasma treatment. The low temperature of the ionic liquid solution during a long treatment time can be explained by the low thermal diffusivity of $[BMI]BF_4$ (see Supporting Information for further discussion). Thus, the complex $[BMI]_2PtCl_4$ can be formed from the Pt compound and $[BMI]BF_4$ under atmospheric pressure plasma, which is different from other plasma systems as previously reported [4,20,21,23]. The complex $[BMI]_2PtCl_4$ can help supplying the buffer space required for the crystallization of Pt [28].

Typical TEM images of the PtNPs at different magnifications are shown in Fig. 1. The heavy element Pt is distinctly observed in Fig. 1(c), where there is lattice spacing in the encapsulated material, and the estimated lattice spacing is 1.96 Å, which coincides well with {200}. Fig. 1(d) shows that the PtNPs have a size of 2-4 nm and mostly 3 nm. The particle size of the PtNPs is close to that of PtNPs synthesized on MWNTs using ionic liquid plasma reduction in our previous study [28]. Other studies using chemical or physical reducing agents had a size of more than 6 nm due to high reduction rate of a modified polyol method by adding silver nitrate [19] or aggregation of PtNPs under laser ablation reduction without SDS [26]. Our PtNPs are not only uniform, but also well distributed without any aggregation on the copper grid. The thin film of ILSM on the surface of the PtNPs is also observed in Fig. 1(b), which was partially



Scheme 1. Schematic diagram of synthesis of PtNPs using plasma reduction.