Structure and morphology of platinum nanoparticles with critical new issues of low- and high-index facets

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Abstract
In this paper, Pt nanoparticles were successfully prepared by modified polyol method using silver nitrate as an effective structure-modifying agent. The characterization of Pt nanoparticles was investigated by using UV-Vis-NIR spectroscopy, transmission electron microscopy (TEM) and high resolution (HR) TEM, and x-ray diffraction (XRD). The method of selected area electron diffraction (SEAD) was used to study the structure of Pt nanoparticles. The results showed that the as-prepared Pt nanoparticles exhibiting the complexity of surface structure and morphology could be used as efficient catalysts for polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs).

Keywords: nanoparticle, structure, morphology, fuel cell

Classification number: 4.02

1. Introduction
So far, Pt nanoparticles with the certain nanostructures, sizes and morphologies have shown significant improvements of catalytic performance in practical applications for proton exchange membrane or polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) \cite{1, 2, 3}. In general aspects, the catalytic and electrocatalytic characterizations of noble metal nanoparticles originate from large surface-to-volume ratio and quantum size \cite{1, 2}. The controlled syntheses of metal nanoparticles with certain sizes, shapes, morphologies, crystal structures and surfaces are highly focused to create new functionalities and utilities for practical applications \cite{1, 2, 3, 4, 5, 6, 7}. Thus, controlling the sizes and morphologies of different crystal facets and large number of atoms on the surfaces, corners and edges can lead to the abilities of tuning the surface sensitivity, activity and selectivity of a catalytic system. Here, the controlled size, structure and morphology of Pt nanoparticles are very crucial in homogeneous and heterogeneous catalysis \cite{1, 2, 7}. Despite the Pt or Pd based catalysts catalyzing most important reactions, they exhibit various and diverse kinds of sizes, morphologies and shapes. With these perspectives, the as-prepared Pt nanoparticles dispersed on carbon nanotubes, oxide matrices are potentially used for catalysts, batteries and fuel cells \cite{2, 3}. Therefore, the electrocatalytic abilities of catalytic enhancement are increasingly improved. Thus, preparing shaped Pt nanoparticles of high efficacy in catalysis for alcohol electro-oxidation is crucial to enable various fuel cell and hydrogen technologies.
In this research, Pt nanoparticles of controlled size and morphology are successfully prepared by polyol method with addition of AgNO$_3$ as modifying-agent. The complexity of surface, surface structure and morphology of Pt nanoparticles are confirmed in our experimental results.

2. Experimental

The chemicals used in our process were bought from Aldrich and Sigma-Aldrich. They were polyvinylpyrrolidone with the chemical formula (C$_6$H$_5$NO) (PVP, MW = 55,000) used as a stabilizer, and chloroformic acid hexahydrate as an important compound (H$_2$PtCl$_6$·6H$_2$O, ACS reagent) used as a good precursor for Pt nanoparticles. Ethylene glycol (EG) (C$_2$H$_4$O$_2$, 95.5%) was used as both the solvent and the reducing agent. Silver nitrate (AgNO$_3$, metal basis, 99.9999%) was used as a structure-modifying agent. In a typical process, chemicals used are poly-vinylpyrrolidone (PVP), chloroformic acid hexahydrate H$_2$PtCl$_6$·6H$_2$O, ethylene glycol (EG), silver nitrate AgNO$_3$, metals basis, ethanol, acetone and hexane, ionized and distilled water by Naranstead nanopure H$_2$O purification system. We used the stock solutions of 3 ml EG and 0.5 ml 0.04 M AgNO$_3$, 2 ml 0.0625 M H$_2$PtCl$_6$, and 4 ml 0.375 M PVP. First, a small volume of 0.0625 M H$_2$PtCl$_6$ of total volume of 2 ml, and a small volume of PVP of 0.375 M, are simultaneously added into the volumetric flask many times (every 60 s or 30 s for a pump), so that a volume of the solution of 0.375 M PVP was more than twice the volume of the solution of 0.0625 M H$_2$PtCl$_6$ (20 µl of H$_2$PtCl$_6$ and 40 µl of PVP via a syringe) until 2 ml of H$_2$PtCl$_6$, and 4 ml of 0.375 M PVP were thoroughly used. The reduction of H$_2$PtCl$_6$ by EG occurring and finishing within 10–30 min was necessary for achieving their sharply polyhedral morphologies. The resultant mixture was heated and refluxed at 160°C for the chemical reduction of H$_2$PtCl$_6$, and the color of the resultant solution became dark-brown. For the polyhedral morphologies, the reduction of H$_2$PtCl$_6$, by EG occurred and was finished within 10–30 min. In contrast, the reduction of H$_2$PtCl$_6$ by EG occurred for 15 min, and the product was kept in the flask for 6 h to obtain non-sharp and non-polyhedral shapes [4, 5]. The fixed volumes were collected for the UV-Vis-near infrared (NIR) measurements. To obtain the fresh Pt nanoparticles without PVP polymer for various measurements, the product was centrifuged at 15,000 rpm for 15 min using a Sigma 3K30C-Kubota centrifuge. The supernatant was separated and precipitated by adding a triple volume of acetone to remove any impurities from outside. We continued to carry out the centrifugation at 12,000 rpm for 30 min again. The precipitate was collected and diluted in 2 ml of ethanol with sonication for 15 min to generate Pt colloidal solution by an ultrasound generator (200 W/37 kHz), and release them randomly in ethanol. Next, 6 ml volume of hexane was added to make the dispersion adequately, and the solution was centrifuged at 3000 rpm for 10 min. To obtain the pure nanoparticles for experimental measurements, the precipitate was washed several times with the same mixture of ethanol/hexane to remove the remaining impurities. After that, the precipitate of Pt nanoparticles was dispersed in 3 ml of ethanol or milli-Q water. Then, the as-prepared Pt nanoparticles were used to study the electroactivity of catalyst electrodes [4, 5]. The TEM and scanning TEM (STEM) images of the pure Pt nanoparticles were obtained using a transmission electron microscopy (TEM) (JEOL JEM-2100F and JEM-2010) operated at 200 kV.

3. Results and discussion

Figure 1(A) showed UV-Vis absorption spectra of PVP-Pt nanoparticles without the centrifugation, 3 ml of ethanol and 30 µl of 0.375 M PVP and 30 µl of the product of the solution containing Pt nanoparticles in respect of their sharp morphologies. They have the specific absorption in the centered range of about 266 nm because the ligand field splitting of PtSd orbital expands the coordination of N and/or O atoms of PVP to Pt$^{4+}$ ions or Pt nanoclusters or Pt nanoparticles. For the solution containing [PtCl$_6$]$^{2-}$ ions (H$_2$PtCl$_6$ in EG), the UV-Vis absorption spectrum showed a strong vibrational peak. The final formation of Pt nanoparticles in the dark-brown solution product of EG and PVP was described by a significant decrease in the absorption bands. This clearly proved the reduction of Pt ions by EG, and indicated the formation of Pt nanoparticles that was protected by PVP polymer [4]. Therefore, the as-prepared Pt nanoparticles under size and morphology control were well...
stabilized by PVP polymer in the extra EG solvent. Clearly, the initial Pt seeds led to Pt clusters, and led to ultra-small size nanocrystals that were formed for a short period of about several minutes.

Finally, the product of PVP-protected Pt nanoparticles was obtained in the extra EG solvent. Figure 1(B) displayed the XRD pattern of the as-prepared Pt nanoparticles, showing the characteristic of the property of the crystalline Pt face-centered cubic (fcc) phase. The peaks were characterized by the first (111) peak, and the next (200), (220), (311) and (222) peaks to the 2θ values of 42.9, 46.4, 67.9, 81.8, and 86.2°, respectively. The XRD peaks of Pt nanoparticles were broad and comparable to those of the corresponding bulk Pt material. By using each XRD peak, the average size of Pt nanocrystallites can be calculated by using the width of the reflection according to the Debye–Scherrer equation: 

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]

where \(\beta\) is the full-width at half-maximum (FWHM) of the peak, \(\theta\) is the angle of diffraction and \(\lambda\) is the wavelength of the x-ray radiation. Here, the (220) reflection of Pt nanoparticles was used to calculate the average particle size according to the Debye–Scherrer formula and the crystallite size [4].

The particle size of polyhedral Pt nanoparticles was analyzed by the TEM method to exhibit the certain 20 nm nanosized range of 8–16 nm in figure 2. Their sizes are nearly homogeneous. They are more than 90% of as-prepared polyhedral Pt nanoparticles (cubic, octahedral, and tetrahedral or truncated cubic, octahedral and tetrahedral) indicating their very sharp corners, edges and facets. Electrochemical data have showed a high catalytic performance for the as-prepared Pt nanoparticles [4, 5]. We suggested that the as-prepared Pt nanoparticles of polyhedral morphologies could be designed as highly efficient catalysts for investigations of the catalytic property in methanol [4, 5]. In addition, there was a typical HRTEM image of one octahedral Pt nanoparticle in figure 2(c). It showed its lattice fringes with the inter-fringe distance \(\sim 0.234\) nm assigned to the inter-fringe distance of the (111) planes belonging to Pt crystal of fcc structure.

In our research, the nano-beam diffraction technique is used to analyze the diffraction pattern of the as-prepared Pt nanoparticles, and the obtained result is presented in figure 3. Figure 3(a) shows a very good SEAD pattern of the sharply polyhedral Pt nanoparticles. The visibly possible \((hkl)\) indices are assigned to a fcc structure of specific \((hkl)\) indices, typically (111), (200), (220), (311), (222), (400), (311), (420), (422), (333), (511), (440), (531), (442), (600), (620) and (533) or more \((hkl)\) according to the selection rule for the various kinds of fcc crystal structures [5, 6]. The planes of (111), (200), (220), (311) and (222) rings were exactly assigned in the XRD data of figure 1(b). The clear SEAD evidences are in good agreement with the XRD data despite the fact that the limit range of the XRD measurement was less than 90°. Therefore, the excellent evidence of \((hkl)\) planes originated from Pt nanoparticles’ defects at surfaces, edges and corners. The as-prepared Pt nanoparticles showed various surface steps, kinks, islands, terraces, and corners [4, 5, 7]. Here, the diffraction peaks and \((hkl)\) planes are referred to in the SEAD pattern in figure 3(b), which experimentally appears in figure 3(a). The differences in the catalytic activity of various morphologies of Pt nanoparticles were confirmed [4, 5]. This also means that the polyhedral Pt nanoparticles exhibited great complexity of surfaces, structure and morphology as well as crystal nanostructures in various atomic arrangements of surface and structure. However, tetrahexahedral Pt nanocrystals with high-index facets have been recently reported to show a high electro-oxidation activity [8, 9]. The tetrahexahedral Pt nanocrystals showed 24 \((hkl)\) high-index facets such as
It is obvious that the surface and internal structure of Pt nanoparticles as well as their shapes and morphologies are relatively complex. At present, they are interesting issues in order to clarify the catalytic activity of Pt catalyst. In particular, the critical issues of durability and stability of Pt based catalysts of the size, morphology and shape as well as the surface change in various chemical environments at low or high temperature and pressure for a long time are crucial. In the experimental evidence, the co-existence of both low-index and high-index crystal facets of the Pt nanoparticles was revealed. Now, it is a challenge to make the only high-index facets or a large number of high-index facets in most of the as-prepared products of noble metal nanoparticles by chemical method with crystal nucleation and growth from solution during their bottom-up synthesis.

4. Conclusions

In this paper, polyhedral Pt nanoparticles were prepared. The as-prepared Pt nanoparticles exhibited complexity of surfaces structure, internal structure, size and morphology with various surface steps, kinks, islands, terraces and corners.

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