Photochemical Synthesis of Composite Noble Metal Nanoparticles for Fuel Cell Catalysts

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Abstract. Direct methanol fuel cell is an ideal way for energy use because of its low noise, simple structure, rich fuel source, low price, easy storage and transportation. However, in the commercial application, it is necessary to overcome high catalyst cost and short life. The work used photochemical reduction and seed crystal growth to reduce Pt¹¹ and Pd¹¹ on the surface of Ag nanoparticles to form Ag@Pt-Pd core-shell composite nanoparticles with particle size of about 5~10 nm. The results showed that the synthesized composite nanoparticles have good electrocatalytic activity, with good research and application in the electrode catalysts of fuel cells.

Keywords: Ag@Pt-Pd, core-shell composite nanoparticles, electrocatalytic activity, fuel cell

1. Introduction
In recent years, precious metal composite nanoparticles have been used in energy, environment, biomedicine and other fields due to their unique structure, and optical, electrical and catalytic properties[1]. It has become the focus of scientific research. Our research group, engaged in the synthesis and application of precious metal composite nanoparticles, has synthesized Au@Ag, Au@Pd, Au@Pt, Pd@Pt, Ag@Pt, etc. Wherein, Au@Pt, Pd@Pt and Ag@Pt show good electrocatalytic activity with further research value[2-4]. However, there are still few reports on the synthesis of three or more components of precious metal nanoparticles at home and abroad, which is still a challenge.

The work used photochemical reduction and seed crystal growth to reduce Pt¹¹ and Pd¹¹ on the surface of Ag nanoparticles, thus forming Ag@Pt-Pd colloid particles. The morphology and size of Uv-vis and TEM were characterized. The results showed that the synthesized colloid was a nanocrystal with core-shell composite structure. The electrochemical properties of the synthesized nanoparticles were studied by using methanol oxidation reaction (MOR) as the evaluation reaction. It was found that the electrocatalytic activity of the synthesized Ag@Pt-Pd composite nanoparticles is due to the traditional Pt nanoparticles, which has good application in fuel cell catalysts.

2. Experiment
2.1. Photochemical preparation of Ag nanoparticles
Add a certain amount of AgNO₃, trisodium citrate, absolute ethanol and acetone in a certain proportion in a volumetric flask to constant volume with water. Then, mix by shaking. The solution was transferred to a quartz reactor and placed on an ultraviolet transilluminator for irradiation. The UV-Vis
spectral curve of the colloidal solution was recorded at intervals of time until two adjacent spectral curves substantially coincided, indicating the complete photochemical reaction. The same method was used to synthesize Pt nanoparticles for comparative experiments.

2.2. Photochemical preparation of Ag@Pt-Pd composite nanoparticles

A certain amount of the Ag colloid was synthesized by Method 1, and the prepared Pt\textsuperscript{II}-Pd\textsuperscript{II} solution was added to the quartz reactor in a certain ratio. The total molar volume of trisodium citrate, ethanol, acetone and precious metals was kept constant, and the molar ratio of Ag to Pt Pd was 1:1. The Pt and Pd molar ratios were 1:4, 1:1 and 4:1, respectively. After uniform oscillation, it was placed on an ultraviolet transilluminators for irradiation. After a period, the UV-Vis spectral curve of the colloidal solution was measured until the spectral curves substantially coincided. That is to say, the photochemical reactions were completely carried out, labeled as Ag@Pt-Pd\textsubscript{1:4}, Ag@Pt-Pd\textsubscript{1:1} and Ag@Pt-Pd\textsubscript{4:1}, respectively.

2.3. Ag@Pt-Pd/C composite nanoelectrochemical analysis

The obtained Ag@Pt-Pd and Pt nanoparticles were loaded on XC-72 carbon black for electrochemical testing. Three-electrode system was used in the electrochemical test, with Pt as the counter electrode, SCE as the reference electrode, the electrolyte of 0.5 mol·L\textsuperscript{-1} KOH+2.0 mol·L\textsuperscript{-1} CH\textsubscript{3}OH, and the temperature of 30-60 °C. The dissolved oxygen in the electrolyte was removed by high purity N\textsubscript{2} gas before the test, and the cyclic voltammetry curve was recorded under N\textsubscript{2} atmosphere. With the test potential range of -0.6 to 0.8 V and the potential scan rate of 50 mV·s\textsuperscript{-1}, the time-current curve (I-t) was tested at the potential of -0.3 V.

In the test, a TEM image of nanoparticles was taken using H-800 transmission electron microscope. Shanghai Jinghua 759MC UV-Vis spectrophotometer was used to record the UV-Vis spectra of nanocolloids. Electrochemical analysis of nanoparticles was performed by Wuhan Corrtest Instrument CS350 Electrochemical Workstation. The precious metal precursor was made of 4N grade. The analytical reagents were used with secondary reverse osmosis demineralized water.

3. Results and discussion

3.1. Characterization of Ag@Pt-Pd composite nanoparticles

Fig. 1a shows the UV-Vis absorption spectrum of Ag colloidal particles. The UV-Vis absorption spectrum of Ag colloidal particles has a distinct characteristic absorption peak around 400 nm, and the colloidal solution turns bright yellow. The Ag@Pt-Pd colloid is brownish black, and the spectrum is a downwardly inclined line from left to right with no characteristic absorption peak. This is similar to the Pt-Pd colloid reported in the literature (See Fig. 1b)[5]. The ultraviolet-visible spectrum of precious metal nanoparticles is generated by the plasmon resonance of the nanoparticle surface, mainly reflecting the surface characteristics of the particles. The plasmon resonance absorption peak of Ag surface has disappeared in the Ag@Pt-Pd colloidal UV-Vis absorption spectrum. There is no Ag on the surface of the colloidal particles. The Ag colloid is encapsulated by Pt and Pd atoms deposited on the surface. The synthesized Ag@Pt-Pd colloid should be a core-shell composite nanostructure.

Fig. 2 shows the TEM image of Ag@Pt-Pd composite nanoparticles. Ag@Pt-Pd colloids are monodisperse near-spherical nanocrystals with the particle size of 5-10nm. Ag@Pt-Pd\textsubscript{1:4}, Ag@Pt-Pd\textsubscript{1:1} and Ag@Pt-Pd\textsubscript{4:1} have average particle diameters of 5.6, 6.8 and 9.4 nm, respectively, larger than the average particle size (4.8 nm) of Ag seed crystals synthesized in this experiment. The average particle size of Ag@Pt-Pd increases with the increased proportion of Pd. There is a clear contrast
between the center of the particle and the surrounding, which may be caused by the difference in imaging between Ag and Pt with Pd in TEM characterization.

3.2. Electrochemical analysis of Ag@Pt-Pd composite nanoparticles

Fig. 3 shows the cyclic voltammogram of Ag@Pt-Pd composite nanoparticles in methanol dissolution. Table 1 shows the current data of oxidation peak of Ag@Pt-Pd_{1:4}/C, Ag@Pt-Pd_{1:1}/C, Ag@Pt-Pd_{4:1}/C and Pt/C at different temperatures.

Table 1 Current peak mA/mg of linear cyclic voltammetry of Ag@Pt-Pd/C catalyst.

| Sample       | 30°C  | 45°C  | 60°C  |
|--------------|-------|-------|-------|
| Pt/C         | 144.6 | 284.2 | 322.6 |
| Ag@Pt-Pd_{1:4} | 262.2 | 491.3 | 692.8 |
| Ag@Pt-Pd_{1:1} | 522.6 | 582.0 | 719.4 |
| Ag@Pt-Pd_{4:1} | 359.4 | 508.8 | 652.9 |
The results showed that for MOR, the electrocatalytic activity Ag@Pt-Pd was higher than that of Pt nanoparticles. Wherein, Ag@Pt-Pd$_{1:1}$ had the optimal activity, about 3.5 times Pt nanoparticles at 30 °C. The peak currents of Ag@Pt-Pd$_{1:4}$ and Ag@Pt-Pd$_{4:1}$ also reached 1.8 times and 2.5 times that of monometal Pt, respectively. We speculated that, on the one hand, the heterogeneous catalytic reaction mainly occurred on the surface of the solid catalyst. The Ag@Pt-Pd composite nanoparticles Pt and Pd atoms in this experiment were deposited on Ag nanoparticles to form a thin shell. This improved the utilization of Pt and Pd, beneficial to the high catalytic activity of the nanoparticles.

On the other hand, we found that the electrocatalytic activity of Ag@Pt-Pd composite nanoparticles was closely related to the molar ratios of Pt and Pd, which is because the valence electron arrangement of Pt was 5d$^9$6s$^1$. Influenced by the relativistic effect, 6s electron contraction led to the increased electron cloud density. The barrier of d-electron hybridization of Pt and Pd atoms was reduced, which facilitated the interaction of Pt atoms with Pd atoms to form a large conjugated system. At the same time, the d% (46) of Pd was slightly larger than that (44) of Pt, so the 4d electrons of Pd could partially flow into the 5d orbit of Pt. The electron donating of the Pd core to the Pt shell improved the amount of d electron holes of Pt and Pd in the shell layer, which was the main reason for the good electrocatalytic activity of Ag@Pt-Pd composite nanoparticles[6-8]. With the increase of temperature, the peak current of each catalyst increased significantly, and the peak current difference of each catalyst gradually decreased. This was due to the fact that MOR was more likely to occur with increasing temperature, and the difference in activity of each catalyst was somewhat reduced.

In addition, the results showed that the cyclic voltammetry curve of Ag@Pt-Pd composite nanoparticles was coincident with a continuous cyclic voltammetry scan of 30 min (See Fig. 3), and the peak current slightly decreased. The electrocatalytic activity of Ag@Pt-Pd composite nanoparticles was relatively stable, and the peak current drop should be the result of continuous oxidation of methanol. Therefore, Ag@Pt-Pd composite nanoparticles have good prospects in the electrode catalysts of fuel cell.

4. Conclusions
1) In the work, Ag nanoparticles were used as seed crystals, with Pt$^{II}$ and Pd$^{II}$ added. Ag@Pt-Pd ternary precious metal nanoparticles with different metal molar ratios were synthesized by photochemical seed crystal growth.

2) TEM characterization showed that the synthesized Ag@Pt-Pd composite nanoparticles were monodisperse near-spherical nanoparticles of 5~10 nm. Combined with UV-Vis spectroscopy, we speculated that the synthesized Ag@Pt-Pd nanoparticles should be a core-shell composite structure.

3) Ag@Pt-Pd ternary precious metal nanoparticles were supported on carbon black Vulcan XC-72 carrier, and their electrocatalytic activity for methanol was analyzed by cyclic voltammetry. The results showed that Ag@Pt-Pd nanoparticles had excellent catalytic activity. Especially at the experimental temperature of 30°C, the peak current of Ag@Pt-Pd$_{1:1}$ reached 522.6 mA / mg$_{\text{Preciousmetal}}$, which was about 3.5 times that of single metal Pt. The effective Pt and Pd utilization and the electron donating of Pd to Pt by Ag core were the main reasons for the high electrocatalytic activity of Ag@Pt-Pd composite nanoparticles. Ag@Pt-Pd core-shell composite nanoparticles have good electrocatalytic activity with prospects in the electrode catalysts of fuel cell.

Acknowledgments

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