

THE FUEL CELL APPLICATIONS OF CHEMICALLY FUNCTIONALIZED GRAPHENE SUPPORTED PLATINUM NANOPARTICLES

Shifeng Hou, Marzena S. Wietecha, Clemonne J. Madarang

Chemistry & Biochemistry, Montclair State University, Montclair, NJ, USA.07058
E-mail hous@mail.montclair.edu

Introduction

Metallic nanoparticles have many applications in catalysis, especially for fuel cells. Graphene has been demonstrated to be a good candidate as a heterogeneous catalyst support to load nanoparticles, organic molecules and biomolecules for the applications in fuel cells, solar cells, super-capacitors and sensors [1-6]. These graphene-loaded nanoparticles were found to show higher electrochemical surface areas and electrochemical catalytic activity with improved stability as compared with the commercial catalysts[6]. In this report, polyethylene glycol (PEG) had been linked to graphene surface. Pt-nanoparticles (Pt-NPs) were synthesized onto PEG modified graphene (PEG-G) sheets and demonstrated that graphene-supported Pt-NPs can show enhanced efficiencies for methanol oxidations compared to graphene and commercial products. Moreover, the Pt-NPs-PEG-G shows higher catalysis activity and longer stability. The electrocatalysis of oxygen reduction using Pt-NPs-PEG-G also shows encouraging behavior.

Experimental

Amino polyethylene glycols, O-(2-Aminoethyl) polyethylene glycol (MW~1000, and 5000) were used to modify graphene oxide. Graphene oxide and reduced graphene oxide were prepared by using Hummers method. The process to link PEG-NH₂ onto graphene surface is demonstrated in Figure 1. Typically, 0.1g graphene was treated with 50ml Thionyl bromide (SOBr₂) to yield Graphene-CO-Br (G-CO-Br), and G-CO-Br was reacted with amino-PEG to yield PEG-G. The product (PEG-G) was obtained by filtration and washing with ethanol, water and HCl sequentially and dried in an oven for future use.

PEG-G supported Pt catalysts were synthesized by mixing 100 mg of PEG-G powder with 1.5 ml of hexachloroplatinic acid in 10 ml of ethylene-glycol (EG) solution and the solution was mechanically stirred for 2 hours. NaOH (2.5 M in EG solution) was added to adjust the pH of the solution to 8.5~9.5, and then the solution was fluxed under flowing argon at 130 °C for 12 hours. The solid was filtered, washed with DI water, and dried in an oven at 80 °C for 12 hours. By varying the mass ratios of platinum to graphene, three PEG-G support Pt nanoparticles with different loading ratios (Mass ratio = (mass of PEG-graphene) : (mass of Platinum)), 1:0.25, 1: 0.5 and 1:1, are synthesized respectively. Similar procedures and parameters were used to prepare graphene and graphite supported Pt catalysts (Pt-NPs-G and Pt-NPs-graphite).

The morphology of catalyst supports Pt nanoparticles, and the distribution of the nanoparticles on different supports were explored using a JEOL JSM-840A scanning electron microscope (SEM) and an FEI Quanta 200 field emission scanning electron microscope (FESEM), equipped with an Oxford INCA 250 silicon drift X-ray energy dispersive spectrometer (EDS).

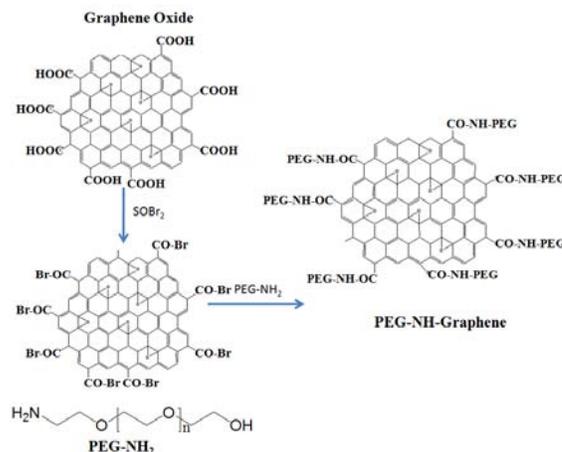


Figure 1 The synthesis process of As-prepared PEG-G

Electrocatalytic activities of Pt nanoparticles on different supports were measured in a conventional three electrode cell using a CHI 600C electrochemical work station. Pt wire worked as a counter electrode, the Saturated calomel electrode (SCE) as a reference electrode, and glassy carbon (3 mm diameter) coated with nanoparticles as a working electrode. To fabricate a working electrode, 5.0 mg of Pt-NPs-PEG-G powder was dispersed in 2 ml of ethanol solution; 2.5 µl of the suspension was placed onto the surface of a glassy carbon electrode and dried for 15 min; and 10 µl of 0.5% Nafion 117 solution (Sigma Aldrich) was sequentially applied and dried for 15 min. The Nafion acted as an adhesive to hold the catalyst membrane to the electrode surface.

Prior to electrochemical characterizations, all electrolyte solutions were deaerated under flowing nitrogen gas for 20 min. Electrocatalytic oxidation of methanol on Pt-NPs-G, Pt-NPs-PEG-G, and carbon black supported Pt NPs were measured in 1 M CH₃OH + 1.0 M H₂SO₄ electrolyte by cyclic voltammetry between -0.2 V and 1.2 V. After methanol oxidation measurements, the electrodes were kept in distilled water for 30 min prior to ethanol oxidation measurements.

Results and Discussion

TEM and SEM was used to characterize Pt-NPs-PEG-G, and Pt nanoparticles with a size of between 3 to 10 nm were observed, which are generated through various synthesis condition. The element analysis from EDS spectrums confirmed that the mass percents of Pt in the Pt-NPs-PEG-G composited are (22±6)%, (44±7)% and (88±6)% respectively, which are in accordance with the initial ratio.

Generally, the reduced graphene shows lower solubility in aqueous solution. However, the as-prepared PEG-G can

disperse into individual graphene sheets in water spontaneously, forming a suspension with long-term stability. And most important, we found that the introduction of Pt – nanoparticles onto PEG-graphene surface did not affect its solubility in water solution. A series of solutions of Pt-NPs-PEG-G with various concentrations were prepared. For example, we found that Pt-NPs-PEG-G can mix with Nafion ethanol solution to form a uniform, high stability suspension. These suspensions can be used as novel electrode materials to fabricate a uniform film on gold and GC electrode surface. In addition, a Pt-NPs-PEG-G film with layered structure and high conductivity has been successfully prepared.

The electrocatalytic activity of methanol oxidation on Pt-NPs-PEG-G, Pt-NPs-G and Pt-NPs-Graphite were characterized by cyclic voltammetry in an electrolyte of 1.0 M CH₃OH and 1.0 M H₂SO₄, respectively. A typical voltammogram of Pt-NPs-PEG-G are shown in Figure 2 a. The efficiencies of the Pt nanoparticles on methanol oxidation were compared in items of forward peak current density, the ratio of the forward peak current density to the reverse peak current density and the oxidation peak. The forward peak current density of methanol oxidation for Pt-NPs-PEG-G is 393.5 mA/mg Pt, and the corresponding ratios of the forward peak current density to the reverse peak current density is 6.02. In comparison to graphene sheets and graphite as catalyst support, PEG-graphene can more effectively enhance electrocatalytic activity of Pt nanoparticles for the oxidation of methanol.

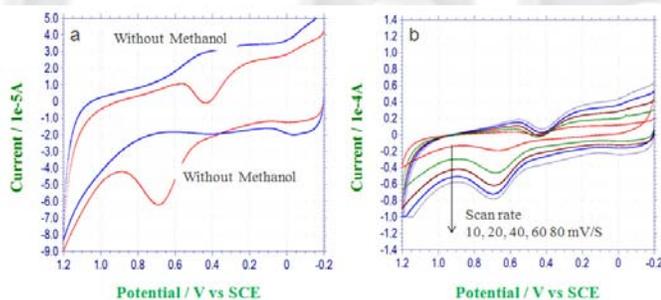


Fig. 2 The cyclic voltammograms of Pt-NPs-PEG-G with and without methanol (a) and Pt-NPs-PEG-G in 1 M CH₃OH/1.0 M H₂SO₄ at different scan rates between -0.2 and +1.2 V vs. SCE (b).

Further investigation had demonstrated that the forward peak current density is proportional to the square root of the scan rate (Figure 2 b), suggesting that the oxidation behavior of methanol at Pt-NPs-PEG-G electrode is controlled by diffusion-process. In addition, the slopes for Pt-NPs-PEG-G are almost as the same as those of Pt-NPs-G but is larger that of Pt-NPs-graphite, which indicates a faster diffusion process of methanol on the surface of graphene sheets and PEG-G than that of methanol on the graphite.

The effect of PEG chains on the morphology of the Pt particles on the graphene surface was also investigated. The Pt nanoparticles with small average size and uniform dispersion could be obtained from PEG-graphene[7]. The investigation of

the reason for the effect of PEG on the morphology of the Pt nanoparticles is ongoing in our groups.

Conclusions

In conclusion, our results demonstrate the presence of PEG on graphene surface can enhance the solubility of graphene in water. Pt nanoparticles were successfully synthesized on PEG-graphene sheets. We have further characterized the compatibility of PEG-graphene with a series of polymer matrices. Our results clearly show that, PEG-graphene supported Pt nanoparticles possess superior electrocatalytic activity than graphene and graphite support. The presence of PEG chains on graphene surface are critical parameter for the development of novel catalyst supports for direct methanol fuel cells. Our findings suggest promising applications for graphene as catalyst supports with the development of large scale production of graphene sheets. The technique developed here can be extended to synthesize various functionalized graphene by using other functional groups. This result should facilitate the preparation of graphene derivatives or the development of graphene-based catalyst materials.

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