

Platinum Nanoparticles Supported on Graphite Nanofibers Prepared by Microwave Irradiation and Its Electrocatalytic Activity

Jie ZHAO¹, Wei Xiang CHEN^{1*}, Gui HAN¹, Yi Fan ZHENG^{1,2}, Zhu De XU¹

¹Department of Chemistry, Zhejiang University, Hangzhou 310027

²College of Chemical Engineering and Materials, Zhejiang University of Technology, Hangzhou 310032

Abstract: Platinum nanoparticles supported on graphite nanofibers (GNFs) were prepared by microwave assistant heating polyol process. TEM images showed that microwave prepared Pt nanoparticles supported on GNFs were small and uniform, and the average diameter was about 3.4 nm. Cyclic voltammetric test showed that Pt/GNFs exhibited very high electrocatalytic activity for methanol oxidation.

Keywords: Platinum nanoparticles, graphite nanofibers, microwave, electrocatalytic activity.

The unique properties of graphite nanofibers have generated intense interest in the application of these new carbon materials toward a number of applications including selective absorption, energy storage, and catalyst supports. The great potential of graphite nanofibers as catalyst support materials has been demonstrated by several researchers¹⁻⁶. Metal particles like Pt, Pd and Ru were applied on graphite nanofibers and the resultant materials showed good catalytic behavior¹⁻³. Recently, it was demonstrated that graphite nanofibers supported Pt and PtRu nanoparticles as the electrode for fuel cell applications showed good electrocatalytic performances⁴⁻⁶.

However, conventional methods for preparing supported metal particles based on the impregnation/reduction and chemical reduction of metal salt precursors do not provide satisfactory control of particle size and high dispersion. As the size and dispersion of metal particles take an important role on their catalytic activity⁷, it is still a challenge with the scientific and technological interesting to synthesis highly dispersed supported metal particles with small and uniform size. As a fast, simple, uniform and energy efficient heating method, microwave irradiation has been applied in chemical reactions⁸ and nanomaterials synthesis⁹⁻¹². Recently, there have been more reports in preparing polymer-stabilized metal nanoparticlae⁹⁻¹⁴ and metal oxide nanoparticles¹⁵ by microwave irradiation. XC-72 carbon supported Pt nanoparticles were prepared by microwave irradiation and showed higher catalytic activity for the electrochemical oxidation of methanol than the commercial E-TEK Pt/C catalyst in the previous work¹⁶.

* E-mail: weixiangchen@css.zju.edu.cn

We herein use the microwave assistant heating polyol process to prepare platinum nanoparticles supported on graphite nanofibers. It was found that the microwave-synthesized platinum nanoparticles were small and uniform in size and highly dispersed on graphite nanofibers. The Pt/GNFs catalyst showed very good electrolytic activity for methanol electrochemical oxidation.

Graphite nanofibers was prepared by dissociating acetylene, using nickel foams as catalyst¹⁷. TEM and HRTEM observations showed that the graphite nanofibers were of the fishbone type graphite layers and their diameter varied from 100-200 nm¹⁷. In order to improve the decoration of metal particles on graphite nanofibers, they were treated with HNO₃ refluxing for 4 h at 373 K. 2.0 mL 0.05 mol/L H₂PtCl₆, 1.5 mL 0.4 mol/L KOH and 0.08 g of the graphite nanofibers were added into 50 mL ethylene glycol in a 100 mL baker. After ultrasonic dispersing them in ethylene glycol, the baker was placed in a microwave oven (National, 2450 MHz, 800W) and heated for 50 s. The product was collected by filtration and washed with absolute acetone, then dried in a vacuum oven at 393 K overnight. The samples were characterized by EDX (JEOL JSM-5600LV), XRD (Philips PW diffractionmeter, CuK α) and TEM (JEM 200CX). Cyclic voltammetry was performed on CHI 660 A potentiostat/galvanostat in a conventional three-electrode cell at room temperature. The working electrode was a thin layer of Nafion-impregnated Pt/GNFs catalyst cast on a vitreous carbon disk electrode. A Pt foil and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The electrolyte was a solution 2 mol/L CH₃OH in 1 mol/L H₂SO₄.

Repeated EDX measurements show the mass fraction of Pt in Pt/GNFs was 18.3%, which agreed with the ratio of Pt to GNFs in the starting mixture. **Figure 1** shows the XRD pattern of Pt/GNFs. All the diffraction peaks of Pt could be indexed using the standard powder diffraction file of Pt (JCPDS number 1-1311). The diffraction peak at $2\theta = 39.7^\circ$ for Pt(111) corresponds well with the interplaner spacing of $d_{111} = 0.227$ nm. Repeated TEM imaging showed that the microwave-prepared Pt nanoparticles were uniformly distributed on GNFs (**Figure 2**). As shown in **Figure 2**, Pt nanoparticles have a narrower particle size distribution. The majority of the Pt particles vary from 3.0 and 4.0 nm and only a few particles larger than 5.0-6.0 nm. The average diameter of Pt nanoparticles was about 3.4 nm. Therefore, it is concluded that microwave heating of the ethylene glycol solution of H₂PtCl₆/KOH/H₂O in the presence of GNFs had evidently promoted the uniform dispersion of Pt nanoparticles on GNFs.

Microwave assisted heating polyol process has been successfully employed to prepare poly(N-vinyl-2-pyrrolidone) (PVP) stabilized Ag, Au, Pd, Ru and Pt nanoparticles⁹⁻¹⁴. At high temperature about 160-180°C, ethylene glycol generated *in-situ* reducing species, CH₃CHO, which reduced the metal ions to their elemental states^{13, 18}. Ethylene glycol with high dielectric constant (41.4 at 298 K) is conducive to rapid heating by microwave irradiation. The fast microwave heating accelerates the reduction of the metal precursor and the nucleation of small metal clusters. The microwave heating also reduces the temperature and concentration gradients in the reaction medium, thereby providing a very homogenous environment for the nucleation and growth of metal particles. Although PVP was not used in this work, carbon materials could act as the stabilizer for Pt nanoparticle. A lot of oxygen functional groups would be

introduced on the surface of GNFs after HNO_3 treatment³. These oxygen functional groups would be suitable for heterogeneous nucleation. The presence of GNFs also interrupted agglomeration of Pt particles. Therefore, the small and uniform Pt nanoparticles dispersed on the surface of GNFs could be achieved by microwave irradiation even if without PVP.

Figure 1 XRD pattern of microwave-synthesized Pt/GNFs

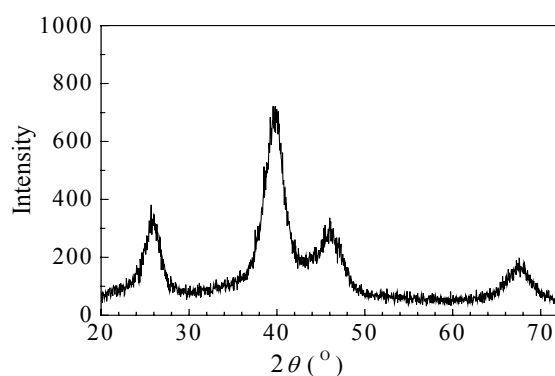


Figure 2 TEM of microwave-synthesized Pt/GNFs

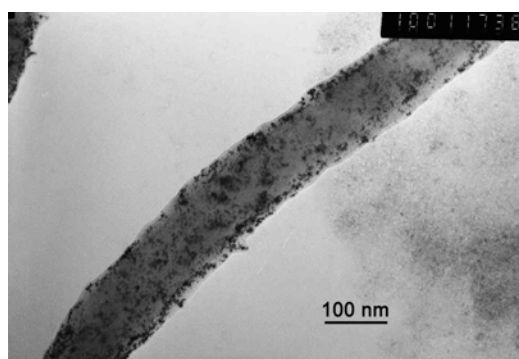


Figure 3 Cyclic voltammograms of methanol electrochemical oxidation over Pt/GNFs electrode in 2 mol/L CH_3OH / 1 mol/L H_2SO_4 electrolyte at 20 mV/s at room temperature

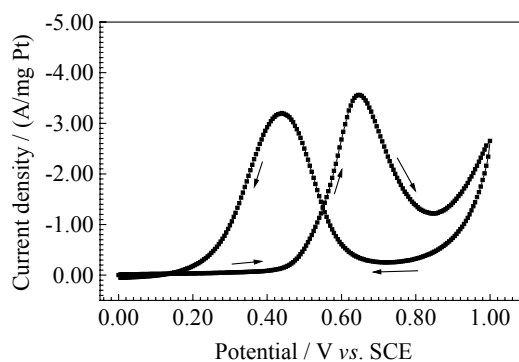


Figure 3 shows the cyclic voltammograms of methanol electrochemical oxidation over microwave synthesized Pt/GNFs catalyst in 2 mol/L CH₃OH/1 mol/L H₂SO₄ electrolyte. The voltammetric feature is in good agreement with most published works^{19, 20}. The current peak at about 0.65 V vs. SCE in the forward scan is attributed to methanol electrooxidation over the Pt/GNFs catalyst. The peak current density is as high as 3.56 A/(mg Pt), which is higher than 3.00 A/(mg Pt) over E-TEK Pt/C catalyst at the same condition¹⁶. The fact indicates that the microwave synthesized Pt/GNFs is very high electrochemically active for methanol electro-oxidation.

A microwave irradiation method for synthesis of platinum nanoparticles supported on GNFs was reported. In conclusion, the platinum nanoparticles generated by microwave irradiation were small and uniform in size, and very well dispersed on the surface of GNFs. GNFs might act as a stabilizer for platinum nanoparticles and interrupts agglomeration of Pt particles. The microwave polyol process for preparing Pt nanoparticles supported on GNFs was rapid, simple and efficient.

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