An XPS study of platinum nanoparticles prepared by a low-pressure flat flame

Huan-Hsiung Tseng, Yu-Chen Chang*

Department of Chemical Engineering and Materials Science,
Yuan Ze University, Taoyuan, Chungli 320, Taiwan, R.O.C.

*** e-mail: yjchan@saturn.yzu.edu.tw**

ABSTRACT

The one-step synthesis and characterization of nanostructured metallic platinum microspheres by a low-pressure flat flame technique is presented here. Field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) analyzed the as-derived powders. Collectively, the results obtained from these analyses confirmed the formation of microspheres comprising closely packed metallic platinum nanoparticles of face center cubic structure. Nanoparticles contained within submicrometer to tens of nanometer microspheres as derived with 0.1 and 0.01M H_2PtCl_6 solution have a volume-averaged size of 14.59 and 12.20 nm as determined by XRD. The XPS analyses confirmed the composition of the surface layer of the microspheres to be metallic platinum.

Keywords: platinum, nanostructure, flat flame, synthesis

INTRODUCTION

At present, Nanometer platinum or platinum alloys are the catalysts of choice for polymer electrolyte membrane (PEM) fuel cells because of their high catalytic activity and their stability in the fuel cell environment. Platinum nanostructures with high specific surface area have wide-ranging applications in numerous technologically important fields such as catalysis, sensor, fuel cell etc. Majority of related literatures reported the synthesis or manufacture of platinum nanostructures based on wet-chemistry based methods. As technological demands and global competition for novel materials with intriguing properties surge, a great number of research teams worldwide (Song et al., 2004; Feng and Puddephatt, 2003; Mayers et al., 2005; Guo et al., 2005) are currently focusing on exploring novel synthesis routes or mechanisms. Among them, Song et al. (2004) prepared 2-D and 3-D dendritic metal nanostructures by a novel photocatalytic seeding approach. In another study by Mayers et al.(2005), hollow nanostructures such as Pt nanotubes and Pt hollow spheres were prepared by templating against selenium nanowires and colloids。 In this study, we report the synthesis of nanostructured platinum microspheres by a novel low-pressure flat flame assisted spray pyrolysis (LPFF-SP) technique. To the best of our knowledge, this is the first paper reporting the preparation of nanostructured platinum microspheres by the combined technique。

EXPERIMENTAL

The physical setup of the flame reactor system employed has been described elsewhere (Chang and Chang, 2002). Analytical grade of hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6{\cdot}6H_2O$, 99.95 %) was purchased from Alfa Aesar (USA) and was dissolved in adequate amount of deionized water to make 0.1 and 0.01M H_2PtCl_6 solutions. The prepared solution was then fed to a 2.4MHz custom-built ultrasonic nebulizer, where the liquid phase precursor was atomized ultrasonically. Droplets thus formed were subsequently carried by a flowing argon gas to a methane-oxygen flat flame stabilized at low pressure inside a vacuum chamber。

For subsequent analyses, particles derived from 0.1 and 0.01M H_2PtCl_6 solutions were both collected on pre-cut silicon wafer substrates. For XPS analysis, particles collected on silicon substrates were used directly. In addition, a 60-μm thick pressed disc of platinum black purchased from Johnson Matthey was also prepared as Pt reference sample。

RESULTS AND DISCUSSION

Figures 1(a) and 1(b) are FESEM micrographs of the particles prepared from 0.1 and 0.01M H_2PtCl_6 solutions, respectively. Note that these are viewed from the edge of the sample specimens, where particles are seen deposited on silicon substrates (as marked). As Figure 1(a) shows, the resulted particles are microspheres of submicrometer to tens of nanometers in size. Further reducing the precursor concentration by one order of magnitude resulted in smaller microspheres as shown in Figure 1(b). Notably, the thickness of the deposited layer is also markedly reduced.

XRD results (in Figure 2.) suggested that both particle samples are platinum of face center cubic structure and the average crystallite sizes derived with 0.1 and 0.01M H_2PtCl_6 solutions were calculated to be 14.59 and 12.20nm respectively.

The photoelectron spectra of particle samples obtained with both precursor concentrations, as well as the platinum black are plotted in Figure 3. The major peaks of all samples analyzed seem to coincide with those of the platinum black. Moreover, the photoelectron line positions are rather close to those reported by Moulder et al.(1995). A scan from 66 to 86 eV for the same samples and platinum black results in spectra and binding energies shown in Figure 4. The result indicates that all samples exhibited binding energies in the 70.62-70.72

and 73.92-74.22eV ranges for Pt $4f_{7/2}$ and Pt $4f_{5/2}$, respectively.

CONCLUSIONS

In summary, we have demonstrated the synthesis of high-purity novel nanostructured platinum microspheres by a low-pressure flat flame technique. Analytical analyses indicate that these microspheres are encompassed with narrowly distributed platinum nanoparticles. Nanoparticles contained within submicrometer to tens of nanometer microspheres as derived with 0.1 and 0.01M H_2PtCl_6 solution have a volume-averaged size of 14.59 and 12.20 nm as determined by XRD. XPS analyses confirmed that the nanoparticles covering the surfaces of these microspheres are metallic platinum。

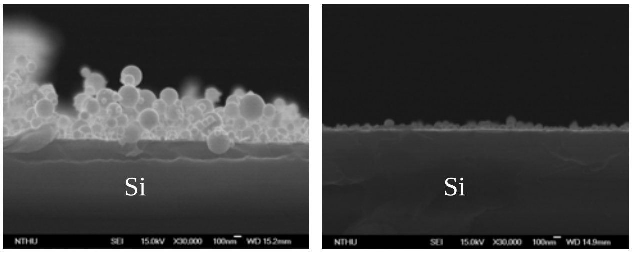

Figure 1. Field-emission scanning electron microscopy of the as-derived particles deposited on silicon substrate (a) 0.1M (b) 0.01M H_2PtCl_6 solution. (Magnification: 30 K at 15 kV)

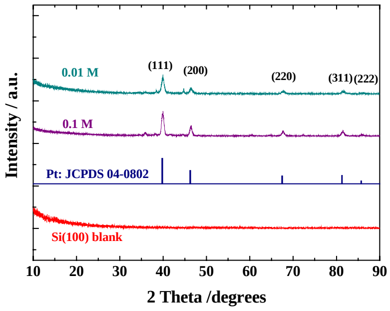

Figure 2. XRD diagrams of microspheres derived from 0.01 and 0.1M H_2PtCl_6 solution.

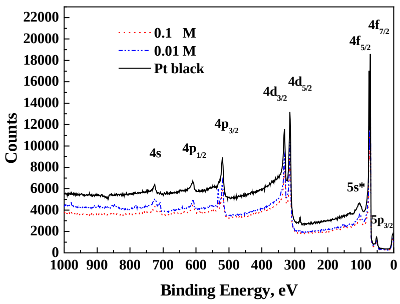

Figure 3. Photoelectron line positions of the as-derived microspheres and Pt black.

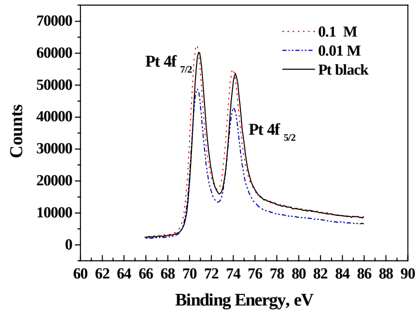

Figure 4. XPS Pt 4f spectra of the as-derived particles and Pt black.

REFERENCES

(1) Song, Y.; Yang, Y.; Medforth, C. J.; Pereira, E.; Singh, A. K.; Xu, H.; Jiang, Y.; Brinker, C. J.; van Swol, F.; Shelnutt, J.A. *J. Am. Chem. Soc.*, **2004** *126*, 635.

(2) Feng, M.; Puddephatt, R. J., *Chem. Mater*, (Communication), **2003** *15*(14), 2696.

(3) Mayers, B.; Jiang, X.; Sunderland, D.; Cattle, B.; Xia, Y. *J. Am. Chem. Soc*., **2005** *125*, 13364.

(4) Guo, X.J.; Yang, C.M.; Liu, P.H.; Cheng, M.H.; Chao, K.J. *Crystal Growth & Design*, **2005** *5*(1), 33.

(5) Chang, Y.C., C.C. Chang, K.Y. Cheng, "Development of A Low Pressure Flat Flame System for Nanoparticle Production," Abstracts of the Sixth International Aerosol Conference, ed. by Chiu-Sen Wang, September 9-13, 2002, Taipei, Taiwan, Volume 1, p547-548.

(6) Wagner, C.D., Riggs W.M., Davis L.E. Moulder J.F., and Mullenberg G.E., Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie. MN 55344 (1979).

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