Preparation of Pt Nanoparticles Assembled in Multilayer Films

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(Received January 7, 2002; CL-020025)

PtCl$_6^{2-}$ anions were assembled on a glassy carbon electrode with [tetrakis(*N*-methylpyridyl)porphyrinato]cobalt cations through layer-by-layer method, then electrochemically reduced to yield zero valent Pt nanoparticles. Regular growth and surface morphology of the multilayer films were characterized by UV/vis, XPS and AFM.

In recent years, the study of nanoparticles of noble metals has been an active area because the metal particles at nanoscale are useful as catalysts and materials with special electronic and optical properties.[1–3] Owing to their unique properties different from bulk materials, many preparation methods of metal nanoparticles have been developed, such as wet-chemistry[4] and electrochemical method.[5] In all these preparation methods, metal nanoparticles dispersed within a polymeric matrix offer attractive routes for combining properties stemming from the inorganic nanoparticle and the polymer.[6,7] However, the metal nanoparticles must be presynthesized by the reduction of a metal salt with a reducing agent in solution in most cases.[8]

In this article, a direct synthetic method of platinum nanoparticles with three dimensional order on a glassy carbon electrode (GCE) based on layer-by-layer (LBL) formation is presented. The preparation route is similar to the strategy used to prepare Pd nanoparticles reported recently.[9] A glassy carbon electrode was first derivatized with 4-aminobenzoic acid (4-ABA) according to the published procedures,[10] and [tetrakis(*N*-methylpyridyl)porphyrinato]cobalt (CoTMPyP) cations and PtCl$_6^{2-}$ anions were alternately assembled by electrostatic interaction. Then, PtCl$_6^{2-}$ anions sandwiched between the CoTMPyP layers were electrochemically reduced applying potential step negatively to yield zero valent Pt particles.

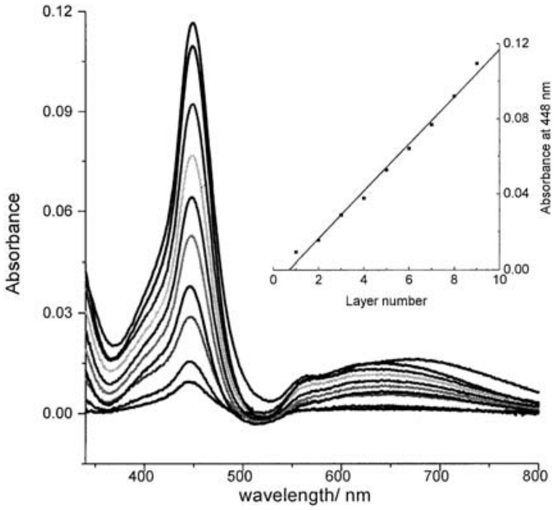

Figure 1. UV/vis absorption spectra of multilayer films (PtCl$_6^{2-}$/CoTMPyP)$_n$ on ITO with $n = 1, 2, 3, \cdots, 8$ and 9 (curves from lower to upper), respectively. The inset shows the relationship of absorbance at 448 nm vs the number of bilayers.

Figure 1 shows the UV/vis absorption spectra of $1, 2, 3, \cdots, 8$ and 9 bilayers of the PtCl$_6^{2-}$/CoTMPyP film on ITO surface, respectively. A characteristic absorption band of CoTMPyP at 448 nm appears. The linear increase in absorbance with the number of layers suggests a regular deposition of the film (Figure 1 inset). After the deposition, the PtCl$_6^{2-}$ anions sandwiched between two CoTMPyP layers of the multilayer films were reduced by electrolysis under constant potential at -0.7 V in an N$_2$-saturated 0.1 M KCl solution. X-ray photoelectron spectrum (XPS) measurements were made to confirm the complete reduction of PtCl$_6^{2-}$ anions and the formation of Pt (0) on multilayer-modified GCE. (The figure not shown.) The Pt (4f$_{7/2}$) and Pt (4f$_{5/2}$) peaks are present at 74.6 and 77.9 eV, respectively, prior to reduction. After electrochemical reduction, both of the peaks shift to 71.4 and 74.7 eV, respectively, which is consistent with the change in oxidation state of platinum from +4 to 0.[11] Importantly, the peak strength of chlorine element weakens greatly after reduction, while the peak strength of other elements such as N and Co has negligible changes. These observations indicate that after reduction, most of the chlorine is released from the metal-ligand, and the rest balances the positive charge of CoTMPyP in the multilayer films.

Atomic force microscopy (AFM) imaging provides more detailed information involving the formation of Pt nanoparticles after electrochemical reduction of PtCl$_6^{2-}$ anions in multilayer films, and the surface morphology and homogeneity of the films. Figure 2 presents AFM images of the multilayer films on (PtCl$_6^{2-}$/CoTMPyP)$_6$/4-ABA/GCE. Before electrochemical reduction (Figure 2A), the modified film exhibites a poor surface morphology because of the relatively rough surface of the glassy carbon. After the film was electrochemically reduced at -0.7 V for 30 minutes (Figure 2B), Pt nanoparticles can be seen clearly. They are homogeneously distributed on the electrode surface. The average diameter of Pt nanoparticles is 6–10 nm. Such Pt nanoparticles in multilayer films exhibit excellent catalytic activity for the reduction of dioxygen. Rotating disk electrode (RDE) voltammetry and rotating ring-disk electrode (RRDE) voltammetry have been carried out, and confirmed that these Pt nanoparticles can catalyze four electron reduction of O$_2$ to water in 0.5 M H$_2$SO$_4$ solution. Thus-prepared noble metal Pt nanoparticles may be used as a promising electrode materials in fuel cell.

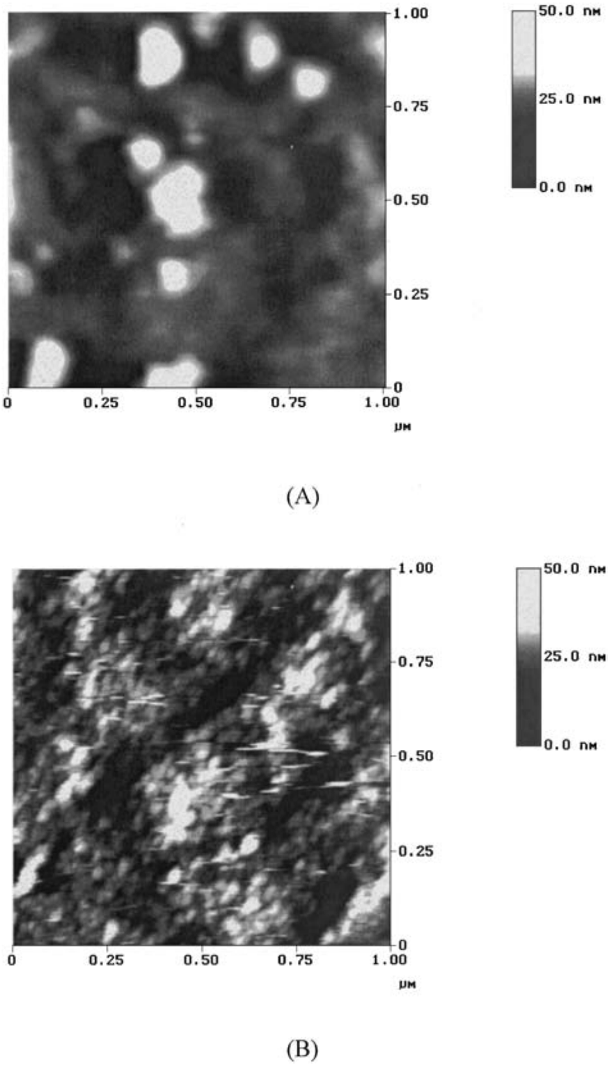

Figure 2. Tapping-made AFM image of a multilayer film $(PtCl_6^{2-}/CoTMPyP)_6$ on a 4-ABA/GC substrate before (A) and after (B) electrochemical reduction.

References and Notes

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