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Dendrimers as nanoreactors to produce platinum nanoparticles embedded in layer-by-layer films for methanol-tolerant cathodes

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Abstract

We report on the fabrication of layer-by-layer (LbL) films of PAMAM dendrimers incorporating platinum nanoparticles (Pt-PAMAM) alternated with poly(vinylsulfonic acid) (PVS). Pt-PAMAM structures were obtained via chemical reduction of H_2PtCl_6 in the presence of PAMAM, using formic acid as reducing agent. An average particle size of 3 nm was estimated using the Scherrer equation with the X-ray diffractograms in multilayer films, which was confirmed with transmission electron microscopy (TEM) for a Pt-PAMAM layer. The formation of Pt nanoparticles was monitored with UV–Vis spectroscopy by measuring the decrease in the band intensity at 375 nm, assigned to the electronic absorption from $PtCl_6^{2-}$ ions. These LbL films were proven fully tolerant to methanol oxidation for potentials below 1.0 V. As a proof of principle, we show that the electrochemical response for the Pt-PAMAM LbL films is characteristic of platinum, regardless of the presence of methanol in the electrolytic solution. The discovery of a methanol-tolerant electrode in Pt-PAMAM LbL films may represent a major breakthrough for further developments in methanol fuel cells, since methanol crossover through the membrane is one of the most important drawbacks of direct-methanol fuel cells.

Keywords: Layer-by-layer; PAMAM dendrimers; Platinum nanoparticles; Methanol fuel cells; Methanol crossover

1. Introduction

Hybrid nanocomposites comprising inorganic particles within an organic matrix have been investigated due to their unique chemical properties [1]. In several cases, the selected organic matrices are the so-called dendrimers, which are highly branched, monodisperse macromolecules, often available in the nanometer size. Dendrimers may undergo a series of chemical modifications and their cavities may serve as templates for nanoparticle growth. Polyamidoamine (PAMAM) dendrimers, in particular, have been used as nanoreactors with effective nanoparticle stabilization [1–3]. For example, hybrid nanoparticles of carboxyl-terminated PAMAM dendrimers containing encapsulated Pt nanocrystals were prepared by Yang et al. [4] and nanoparticles of Au, Cu, and Pd have been produced within PAMAM dendrimers [3].

As far as fuel cells are concerned, the importance of platinum nanoparticles is indisputable [4–9]. For instance, Ye and Crooks [9] have shown that Pt-PAMAM is a catalyst for electroreduction of oxygen. In addition, platinum–ruthenium alloys are the best catalysts for direct methanol fuel cells [5,6]. Platinum is also a good electrocatalyst for methanol oxidation and efficient in oxygen reduction,

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being suitable as a cathode in low-temperature direct methanol fuel cells [7]. One limitation though is the methanol oxidation at the platinum cathode due to the methanol crossover through the Nafion® membrane normally employed in fuel cells. This promotes depolarization of the cell [8] causing power losses. Therefore, it would be interesting if cathode materials were found to prevent such effects.

In this work, we report on the fabrication of layer-by-layer (LbL) films with alternating layers of nanoparticle-containing amine-terminated G4 PAMAM dendrimers (Pt-PAMAM) and poly(vinylsulfonic acid) (PVS). Nano-sized Pt nanoparticles were grown in the presence of PAMAM molecules and the LbL films were employed as methanol-tolerant cathodes for oxygen electroreduction.

2. Experimental

2.1. Synthesis of Pt-PAMAM nanohybrids

Pt-PAMAM nanohybrids were prepared as follows: 2 mL of H_2PtCl_6 solution (1 mmol L^{-1}) were added to 2 mL of PAMAM (0.07 mmol L^{-1}) and 2 mL of formic acid (1 mmol L^{-1}). The final solution (Pt-PAMAM) was kept in the dark during 4 h and then used in film preparation. Pt-PAMAM/PVS LbL and cast films were assembled onto hydrophilic glass, ITO-coated glass, Au-coated glass, and silicon substrates. The concentration of the dipping solutions was set at 0.07 mmol L^{-1} and 0.5 g L^{-1} for Pt-PAMAM and PVS, respectively.

2.2. Layer-by-layer film fabrication and characterization

The sequential deposition of LbL multilayers [15] was carried out in a HMS series programmable slide stainer (Carl Zeiss, Inc.) by immersing the substrates alternately into the Pt-PAMAM and PVS solutions for 5 min. After deposition of each layer (Fig. 1a), the substrate/film system was rinsed and dried with N_2. Ultraviolet–visible (UV–Vis) absorption spectra of the samples were obtained with a Hitachi U-3501 spectrophotometer (Fig. 1b). Film morphology analyses (Fig. 1c) were carried out with an atomic force microscope (AFM) Nanoscope III (Digital Instruments). Fourier transform infrared spectroscopy (FTIR) measurements were performed in films deposited onto Si substrates using a Nicolet 470 Nexus spectrometer, with the sample chamber purged with N_2 gas (Fig. 1d).

The morphology and particle size distribution (Fig. 2) were characterized by means of a 200-kV transmission electron microscope (Philips CM200). The particle size distribution was estimated by the measurement of at least 200 particles in TEM images. The TEM samples were prepared by wetting carbon-coated copper grids with a drop of the Pt-PAMAM suspensions for 10 min followed by drying on air.

2.3. Electrochemical measurements

Cyclic voltammograms (Fig. 3) were obtained in films containing 10 Pt-PAMAM/PVS bilayers deposited onto ITO-covered substrates using an AUTOLAB PGSTAT

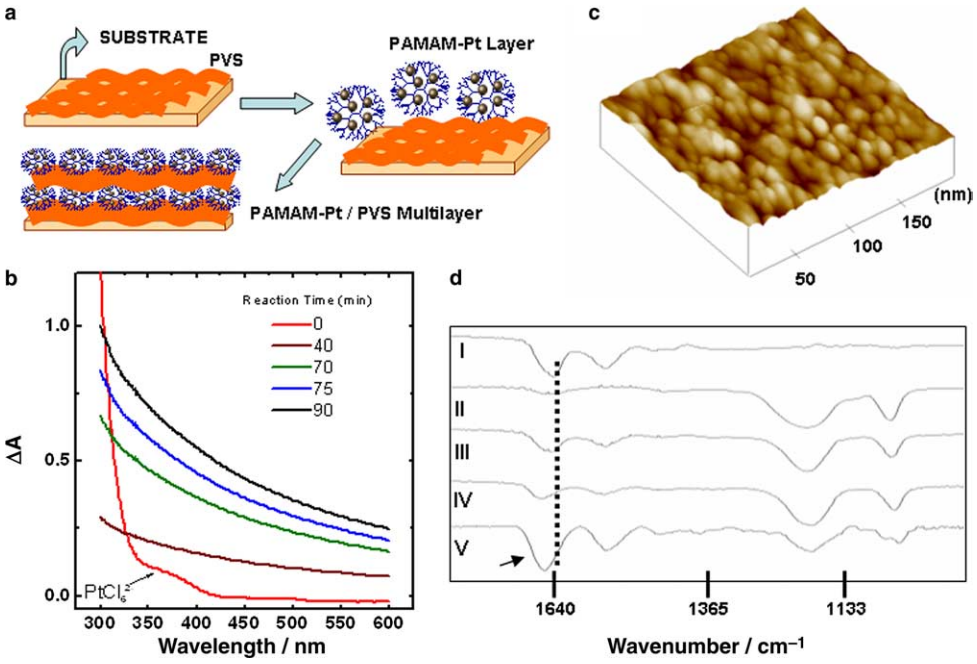

Fig. 1. (a) Idealized structure of Pt-PAMAM/PVS LbL films. (b) UV–Vis spectra of the solution containing PAMAM, H_2PtCl_6 and formic acid, before ($t = 0$) and after several times allowed for reduction of Pt ions. (c) Atomic force microscopy (AFM) image of a 10-bilayer Pt-PAMAM/PVS LbL film onto a glass substrate. (d) FTIR spectra for films of: (I) PAMAM cast; (II) PVS cast; (III) PAMAM + PVS cast; (IV) PAMAM-Pt/PVS cast; (V) 10-bilayer Pt-PAMAM/PVS LbL film.