

Electrostatic layer-by-layer assembly of platinum-loaded multiwall carbon nanotube multilayer: A tunable catalyst film for anodic methanol oxidation

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Abstract

A simple layer-by-layer (LBL) electrostatic adsorption technique was developed for deposition of films composed of alternating layers of positively charged poly(diallyldimethylammonium chloride) (PDDA) and negatively charged multiwall carbon nanotubes bearing platinum nanoparticles (Pt-CNTs). PDDA/Pt-CNT film structure and morphology up to six layers were characterized by scanning electron microscopy and ultraviolet-visible spectroscopy, showing the Pt-CNT layers to be porous and uniformly deposited within the multilayer films. Electrochemical properties of the PDDA/Pt-CNT films, as well as electrocatalytic activity toward methanol oxidation, were investigated with cyclic voltammetry. Significant activity toward anodic methanol oxidation was observed and is readily tunable through changing film thickness and /or platinum-nanoparticle loading. Overall, the observed properties of these PDDA/Pt-CNT multilayer films indicated unique potential for application in direct methanol fuel cell.

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Keywords: Layer-by-layer assembly; Carbon nanotubes; Anodic methanol oxidation

1. Introduction

Direct methanol fuel cells (DMFCs) are considered one of the most promising power sources for applications in electric vehicles and electronic portable devices, due to their high power density, relatively quick startup, rapid response to varying loading, and low operating temperature [1–3]. Carbon nanotubes are used intensively and increasingly as supports for platinum and platinum-alloy catalysts in DMFCs because of high surface area, conductivity and chemical stability [4–6]. Depositing platinum-loaded carbon nanotube (Pt-CNT) films on conducting substrates is a crucial step in constructing DMFCs. Drop-casting has been a standard technique for applying Pt-CNT paste film on

the conducting substrate [4–6]. An electrophoretic method has been reported to afford partially-oriented Pt-CNTs films, with improved DMFCs performance [7]. However, these Pt-CNT films were non-uniform and difficult to control.

Recently, layer-by-layer (LBL) self-assembly of ultrathin films via alternate deposition of oppositely charged polyelectrolytes [8] has attracted increasing interest. This versatile strategy can produce nano-composite films of exceptional uniformity, and the process is highly controllable when using a variety of building blocks, including CNT [9–15]. However, reports of LBL self-assembly of Pt-CNT multilayer film are rare [16] and this technique has not yet been reported for application to DMFCs.

Herein, LBL self-assembly was used to assemble the homogeneous stable Pt-CNT multilayer films on glassy carbon (GC) electrodes, based on electrostatic attraction between positively charged poly(diallyldimethylammonium chloride) (PDDA) and negatively charged CNTs loaded with 3–6 nm platinum nanoparticles. Pt-CNT multilayers prepared in this manner are highly electrocatalytically active toward methanol oxidation. Further,

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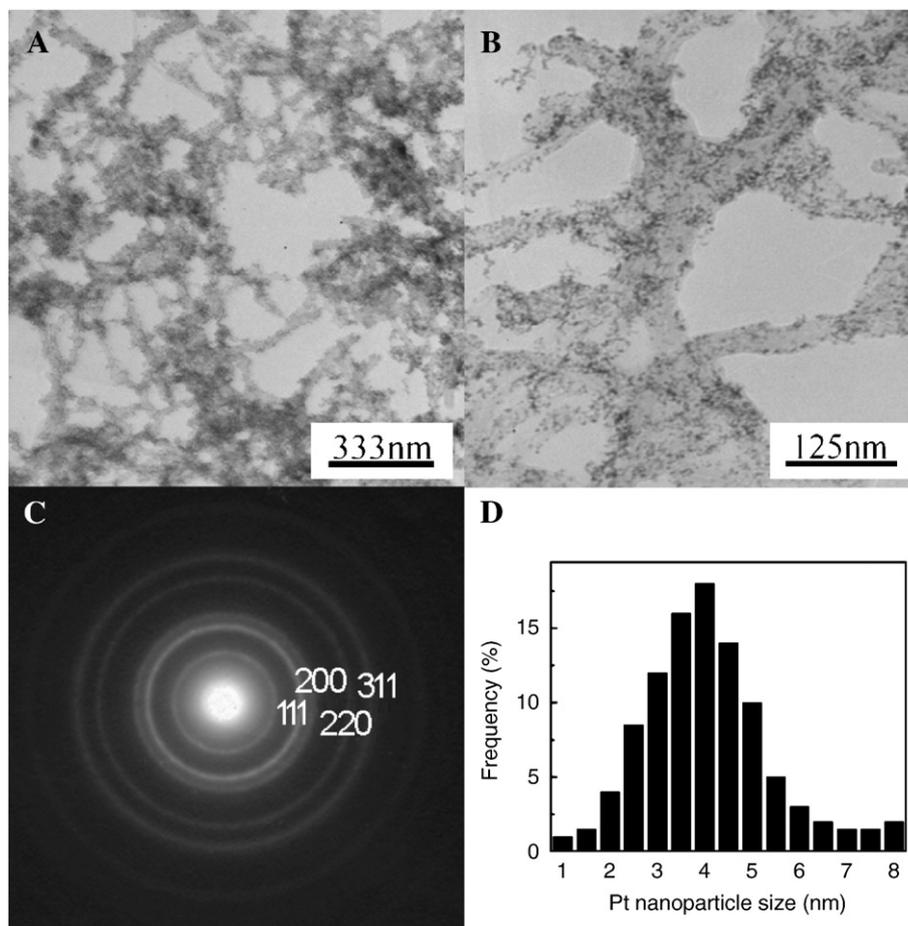


Fig. 1. TEM images of 30 wt.% platinum nanoparticles loaded on sonochemically treated MWNTs: (A) at a low magnification and (B) at a high magnification. (C) Selected-area electron diffraction pattern over several platinum nanoparticles loaded on carbon nanotubes. (D) Particle size distribution for the platinum nanoparticles loaded on carbon nanotubes.

the activity is tunable by changing film thickness and platinum nanoparticle loading on the CNTs.

2. Experimental details

2.1. Preparation of Pt-CNTs

Pt-CNTs were synthesized by thermal reduction of platinum precursor on sonochemically treated multiwalled carbon nanotube [Float1]s (MWCNTs) in an ethylene glycol-water solution [7]. In brief, 10 mg MWCNTs (~5 μm length, 10–30 nm diameter, and 95% purity from Shenzhen Nanotech Port Co, Ltd. China) was stirred and dispersed in a mixed acidic solution of 8.0 M HNO_3 (65%) and 8.0 M H_2SO_4 (98%). The mixture was sonicated in an ultrasonic bath at 60 $^\circ\text{C}$ for 2.5 h, then MWCNTs were recovered by centrifugation and washed successively with deionized water until eluate pH reached 7, and dried in a vacuum oven. Subsequently, a specific amount of dry MWCNTs was suspended in 15 mL of 2:1 ethylene glycol: water, followed by addition of the appropriate volume of 0.01 M aqueous K_2PtCl_6 to achieve the desired Pt-on-MWCNT wt.% loading. The mixture was refluxed under nitrogen at 125 $^\circ\text{C}$ for 2 h, during which time Pt was reduced and deposited as

nanoparticles on MWCNT surfaces. Pt-loaded MWCNTs were then separated by centrifugation and washed thoroughly with deionized water.

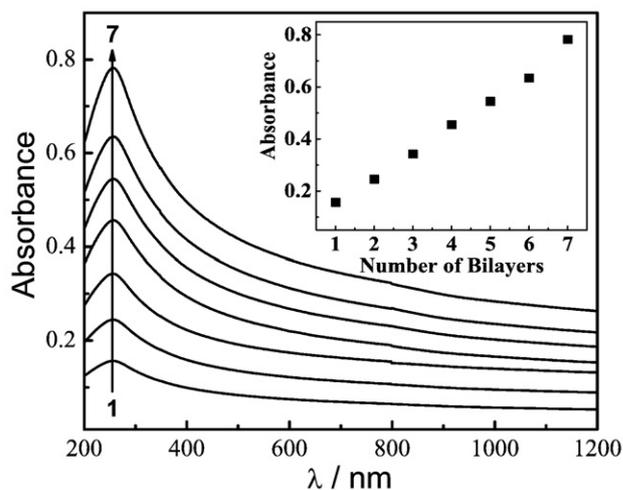


Fig. 2. UV-vis absorption spectra of PDDA/Pt-CNT multilayer deposited on quartz glass slide with various bilayers, Pt-CNT served as the outmost layer. Inset shows a plot of absorbance at 270 nm vs. bilayer numbers.

2.2. Substrate pretreatment and LBL deposition

The substrates used here for LBL deposition were quartz glass and silicon slides (for characterization) and 0.8-mm GC electrodes (for electrochemical studies). Quartz glass and silicon slides were pretreated by immersion in fresh Piranha solution (1:3 30% H_2O_2 /98% H_2SO_4) at 80 °C for 1 h (caution: piranha solution must be treated with extreme care), then washed with deionized water and ethanol and dried under nitrogen gas. GC electrodes (0.8 mm diameter) were polished first with emery paper and then with aqueous slurries of fine alumina powder (1 and 0.05 μm) on a polishing cloth, and finally rinsed with deionized water in an ultrasonic bath for 5 min.

PDDA/Pt-CNT multilayers were deposited via alternately dipping substrate in 1 wt.% aqueous positively-charged PDDA containing 1.0 M NaCl for 30 min and 1.0 gL^{-1} aqueous negatively-charged Pt-CNTs for 1 h. Between dips, the films were rinsed carefully with deionized water to remove unabsorbed materials, then dried with nitrogen gas.

2.3. Characterization

Pt nanoparticle size distribution and Pt-CNT composite morphology were observed using a JEOL 2000 transmission electron microscope (TEM, JEOL, Ltd, Japan) with 200 kV accelerating voltage. Pt-CNT TEM samples were prepared by

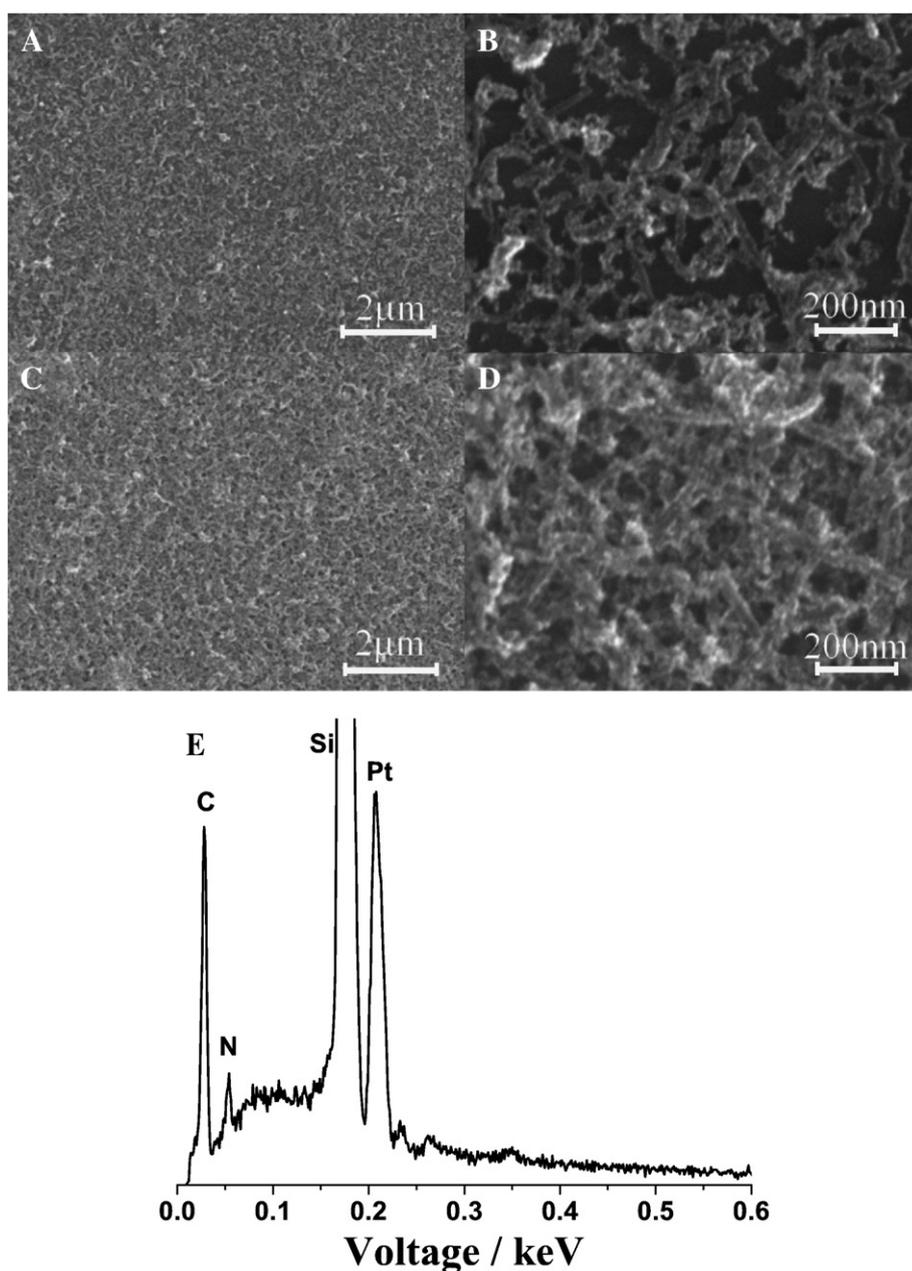


Fig. 3. SEM images of $(\text{PDDA/Pt-CNT})_2$ (A and B) and $(\text{PDDA/Pt-CNT})_6$ (C and D) deposited on silicon slides at low magnification (A and C) and at high magnification (B and D). (E) Energy-dispersive X-ray spectrum of $(\text{PDDA/Pt-CNT})_6$.

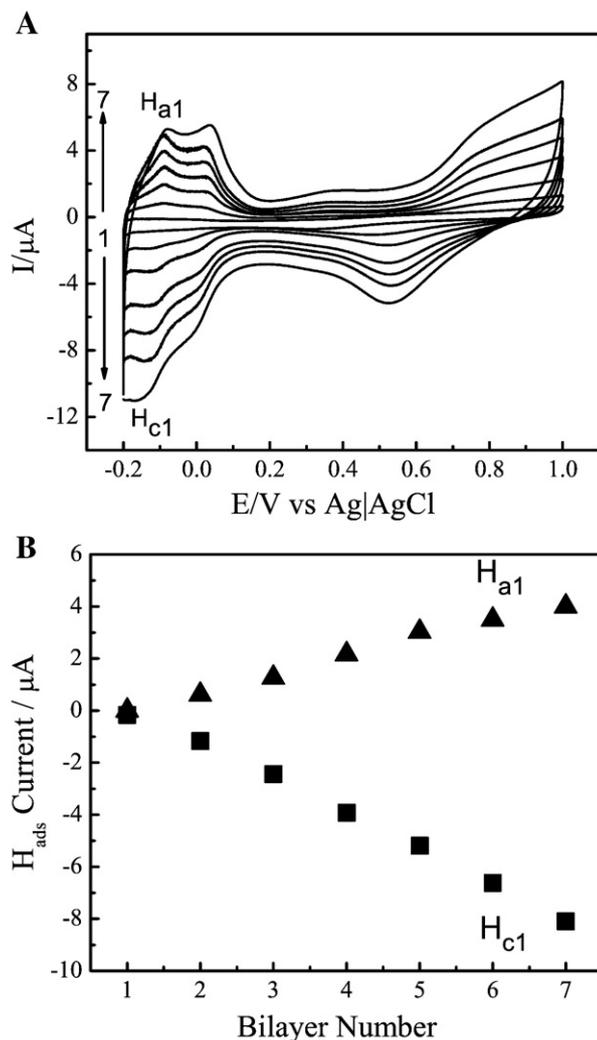


Fig. 4. (A) Cyclic voltammograms (PDDA/Pt-CNT)_n multilayer films deposited on GC electrode in N₂-saturated 0.5 M H₂SO₄ solution. (B) Dependence of H-adsorption current on bilayer number of (PDDA/Pt-CNT)_n. Scan rate: 0.1 V·s⁻¹.

ultrasonic dispersal in ethanol for 5 min, after which 5 μL was dropped onto 400 mesh carbon-coated copper grid and allowed to evaporate in air at room temperature.

LBL deposition of Pt-CNTs on pretreated quartz glass slides was monitored by ultraviolet-visible-near-infrared spectroscopy, using a CARY500 UV/vis/near IR spectrophotometer (Varian, Inc, USA). Multilayer surface morphology was imaged on pretreated silicon slides using an XL30 environmental scanning electron microscope (Philips Electron Optics) with finite element model and 20 kV accelerating voltage. The XL30 ESEM was equipped with energy-dispersive X-ray spectroscopy (EDS), which allowed recording of the composition of the multilayers (line scan at 12 kV accelerating voltage).

Electroactivity of Pt-CNT multilayers toward methanol oxidation was measured by cyclic voltammetry at room temperature, using a CHI660a instrument (CHI, USA) equipped with a three-electrode cell. Measurements were performed in deoxygenated 0.5 M H₂SO₄ solution containing 1.0 M methanol, using a PDDA/Pt-CNT multilayer-coated GC electrode as working electrode, a platinum wire counter electrode, and an Ag|AgCl (in a

saturated KCl solution) reference electrode. All the potential values reported here are relative to the Ag|AgCl reference.

3. Result and discussion

Fig. 1(A, B) shows typical TEM images of Pt-CNTs prepared with 30 wt.% platinum loading. Pt nanoparticles appear uniformly dispersed on MWCNT surface, with average size 3.9 ± 0.8 nm, distributed across the range 2–6 nm (Fig. 1D). Selected-area electron diffraction (SAED) patterns from several platinum nanoparticles loaded on MWCNTs reveals a ring pattern indexed as (111), (200), (220), and (311) of face-centered-cubic (fcc) platinum lattice (Fig. 1C).

Fig. 2 shows UV–vis spectra collected during alternating deposition of PDDA and 30 wt.% Pt-nanoparticle-loaded CNTs on quartz glass slides. Linear increases in MWCNT absorbance at 270 nm [11] with each dipping cycle indicate uniform deposition of Pt-CNT layers.

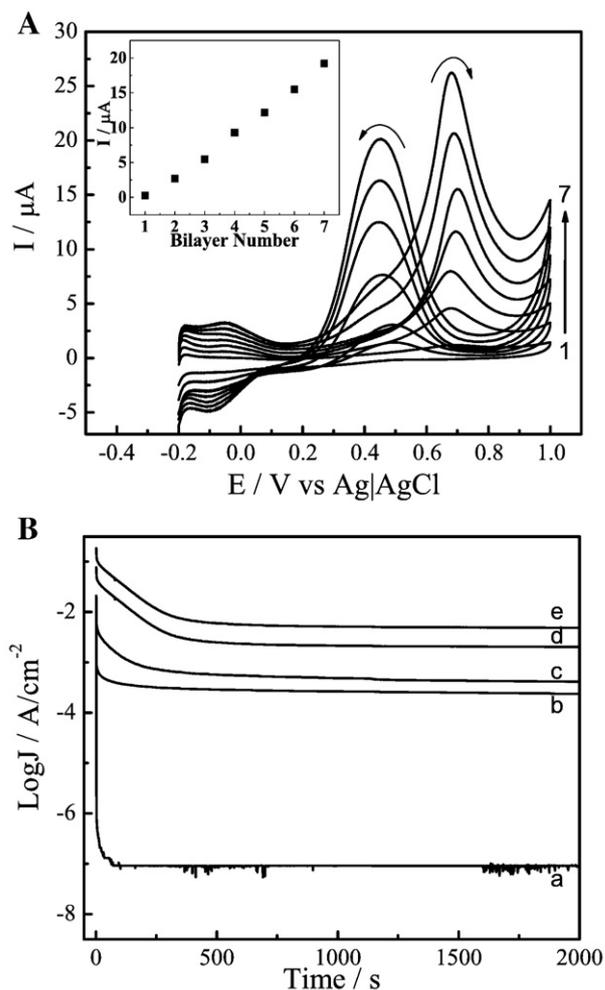


Fig. 5. (A) Cyclic voltammograms (PDDA/Pt-CNT)_n multilayer films deposited on GC electrode in N₂-saturated 0.5 M H₂SO₄ solution containing 1 M methanol. Inset shows catalytic peak current of methanol oxidation at 0.7 V (scan rate: 0.1 V·s⁻¹). (B) Current-time curves for methanol oxidation at a. glass carbon, b. polycrystalline platinum and (PDDA/Pt-CNT)₇ multilayer electrodes with c. 10% d. 20% and e. 30% platinum loaded on carbon nanotubes, respectively.

Typical low-magnification SEM images of (PDDA/Pt-CNT)₂ and (PDDA/Pt-CNT)₆ multilayers, deposited uniformly over the entire surface of the silicon slides, are shown in Fig. 3A and 3C, respectively. Such adsorption uniformity can be attributed to electrostatic attraction between the positive PDDA and the negative Pt-CNTs during dipping. Drop-casting methods have been widely used in the manipulation of carbon nanotube paste, where the carbon nanotubes are mainly in the form of aggregates or indiscernible bundles. Thus, MWCNT films prepared by drop casting are always non-uniform [17]. Higher-magnification images (Figs. 3B and D) clearly shows uniformly distributed Pt-CNTs, overlapping in homogenous, porous and multilayer films. EDS measurements (Fig. 3E) confirm the nanoparticles decorating MWCNTs to be platinum.

The electrochemical properties of the PDDA/Pt-CNT multilayer films were investigated by voltammetry. Fig. 4 shows typical cyclic voltammograms of PDDA/Pt-CNT multilayer films on GC electrodes in nitrogen-saturated 0.5 M H₂SO₄ solution. The oxidation and reduction potentials of platinum nanoparticles occur at 0.70 V and 0.55 V, respectively. In addition, the cathodic and anodic peaks present between -0.20 V and 0.10 V may be ascribed to the redox of atomic hydrogen adsorbed on the surfaces of platinum nanoparticles in acidic media. The linear increase of H-adsorption current with the growth of PDDA/Pt-CNT multilayer (Fig. 3B) is consistent with the results of UV-vis and SEM, which demonstrate the PDDA/Pt-CNT multilayer film was growing uniformly.

The electrocatalytic properties of Pt supported on MWCNTs for methanol oxidation were characterized by cyclic voltammetry obtained in nitrogen-saturated 0.5 M H₂SO₄/1 M CH₃OH solution (Fig. 5A). As reported elsewhere, the Faradaic current of PDDA/Pt-CNTs multilayer films exhibits a well-known dependence on the applied potential for methanol oxidation reaction on carbon materials-supported Pt catalysts [18–20]. In our case, methanol oxidation was representative at the anodic peak around 0.70 V, and the absorbed intermediates produce a second oxidation wave at 0.45 V in reverse scan. Furthermore, the peak current at 0.70 V is directly proportional to the platinum loaded in the PDDA/Pt-CNT multilayer film. Thus, a high catalytic performance toward methanol oxidation can be achieved by increasing the PDDA/Pt-CNT multilayer film thickness. Furthermore, a high catalytic performance toward methanol oxidation can be also achieved by tuning the content of platinum loaded on the carbon nanotube. Fig. 5 B illustrates the current–time behavior for the oxidation of methanol at glass carbon, bulk platinum and (PDDA/Pt-CNT)₇ multilayer film with various platinum loading on carbon nanotube (at 0.7 V). The current–time curves are the log of the current density over a time period of 2000 s in the nitrogen saturated 0.5 M H₂SO₄ + 1 M CH₃OH solution. The catalytic current for methanol on (PDDA/Pt-CNT)₇ multilayer film increase with the content of platinum nanoparticles loaded on MWCNTs which is consistent with the increasing platinum loaded in the PDDA/Pt-CNT multilayer film. In addition, the catalytic activity of (PDDA/Pt-CNT)₇ multilayer films is 0.5–1.5 order of magnitude great-

er than that of bulk platinum, which is attribute to the great catalytic surface of platinum nanoparticles on MWCNTs [4,5]. On the other hand, the current decreases dramatically in the initial stage, then, a constant current was obtained after 500 s, and can remains 5 h polarization at 0.7 V, which demonstrate that the PDDA/Pt-CNTs multilayer films are remarkably stable for methanol oxidation.

4. Conclusion

In sum, an electrostatic layer-by-layer self-assembly technique has been developed for fabrication of platinum-loaded carbon nanotubes film. PDDA/Pt-CNT multilayer films prepared through alternating adsorption of positively charged PDDA and negatively charged Pt-CNT nanocomposites showed high electrocatalytic activity and chemical stability toward methanol oxidation. Due to promising properties such as nanoporous microstructure, uniform integrity, ease of preparation, and readily controllable platinum loading, the PDDA/Pt-CNT multilayer film shows unique and potential for application in DMFCs.

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