Nanostructures

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One-Dimensional Porous Carbon/Platinum Composites for Nanoscale Electrodes**

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Nanostructured carbon materials, especially one-dimensional (1D) carbon nanotubes (CNTs), are of great interest for the development of nanoelectronics, catalytic reactors, and gas sensors.[1–3] Recently, work has focused on the dispersion of metal (usually platinum) nanoparticles in CNTs for applications as electrodes for fuel cells.[4] It is known that the efficiency of the catalyst is low in the case of the ink process for assembling membrane electrodes because of the difficulty of accessing inner electrocatalytic sites.[4c] Metal-incorporated CNTs are expected to circumvent this problem because of their 1D porous structures and good electronic conductivities. However, most of the CNTs synthesized so far exhibit either graphitic or amorphous tubes where the pores in the wall are too small for application in electrocatalysis.[5] Mesoporous CNTs (pore size > 2 nm) can contain a large surface area with good accessibility of the pores, which makes them promising candidates for electrocatalytic applications.

Miniaturized fuel cells have the advantages of high energy density and low operating temperatures.[6] The preparation of submicrometer or nanoscale carbon-supported electrodes with large surface areas is therefore essential. However, the controlled formation of metal-particle-loaded mesoporous CNTs (MPCNTs) to produce a working electrode remains a nontrivial task, but several methods for their preparation have been reported.[7] In this respect, MPCNTs prepared by pyrolysis of hyperbranched polyphenylenes (see Figure S1 in the Supporting Information) are interesting as nanoscale electrodes because of their high porosity and easily graphitized carbon structures.[7a] Moreover, the precursor used has a low melting point ($< 40\,^{\circ}$C) and is polymerizable through heat treatment or irradiation, which may be convenient for the fabrication of miniaturized fuel cells.

Platinum nanoparticles adsorbed on different carbon supports are still considered to be the most efficient catalysts for cathode materials in a fuel cell.[8] Colloidal and impregnation methods have been used in the traditional preparation of highly dispersed platinum clusters on such supports.[8b] With the colloidal method, the size and shape of the clusters are controlled.[9] However, it is difficult to eliminate ligands from the surface of the resulting electrocatalyst without affecting the size and shape of the clusters. In contrast, the impregnation method is simpler and cheaper than the colloidal method, but control of the size and dispersion of the clusters is more challenging.[10]

Herein, we report a novel approach to assemble highly porous platinum/carbon composites in a controlled fashion. Platinum-loaded, 1D MPCNTs (Pt/MPCNTs) with surface areas greater than 1100 $m^2 g$ were prepared by electrochemical deposition of platinum nanoparticles in the pores of the MPCNTs. In contrast to the conventional methods,[11] this method prevents agglomeration of the particles and increases the lifetime of the device. Furthermore, the amount of metal loading can be tuned by varying the concentration of the chloroplatinic acid solution.

Similar to the procedure described elsewhere,[7a] a porous alumina membrane was selected as a template. An alumina membrane filled with MPCNTs was prepared by pyrolysis of hyperbranched polyphenylene at 700 °C in the template and then a gold film (100 nm thick) was evaporated onto one side of the MPCNT/alumina membrane. The surface of the MPCNT was electrochemically modified with 4-aminobenzene,[12] and platinum nanoparticles were electrodeposited at -0.6 V versus the saturated calomel electrode (SCE, Figure 1).

After removal of the alumina template using an aqueous solution of sodium hydroxide (0.1M), large scale arrays of Pt/MPCNTs were observed (Figure 2a). The tubes were aligned and had diameters of approximately 200 nm and a length of up to 60 μm. Compared to the original MPCNTs with smooth wall structures (see Figures S2 and S3 in the Supporting Information), the Pt/MPCNTs showed rough wall surfaces with a large number of particles distributed on them (Figure 2b).

Characterization of the Pt/MPCNTs by transmission electron microscopy (TEM) disclosed that the nanoparticles were dispersed homogeneously, not only on the surface of the tube but also inside the pores of the tube wall (Figure 3). The nanoparticles have a narrow size distribution that ranges from 2 to 5 nm; this range includes the optimal particle size for the highest mass activity for oxygen reduction by platinum

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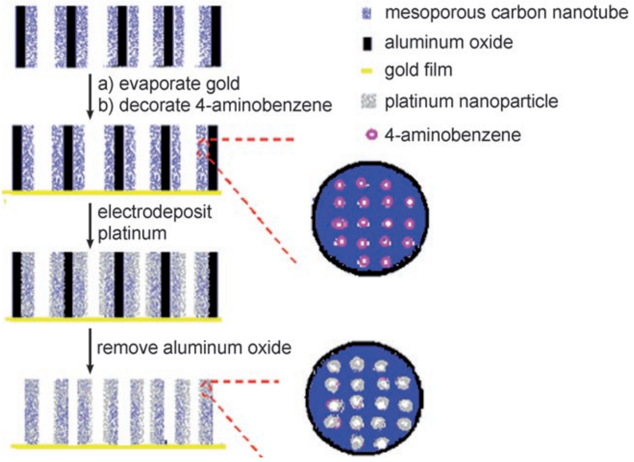

Figure 1. Procedure for the preparation of the platinum/MPCNT composite.

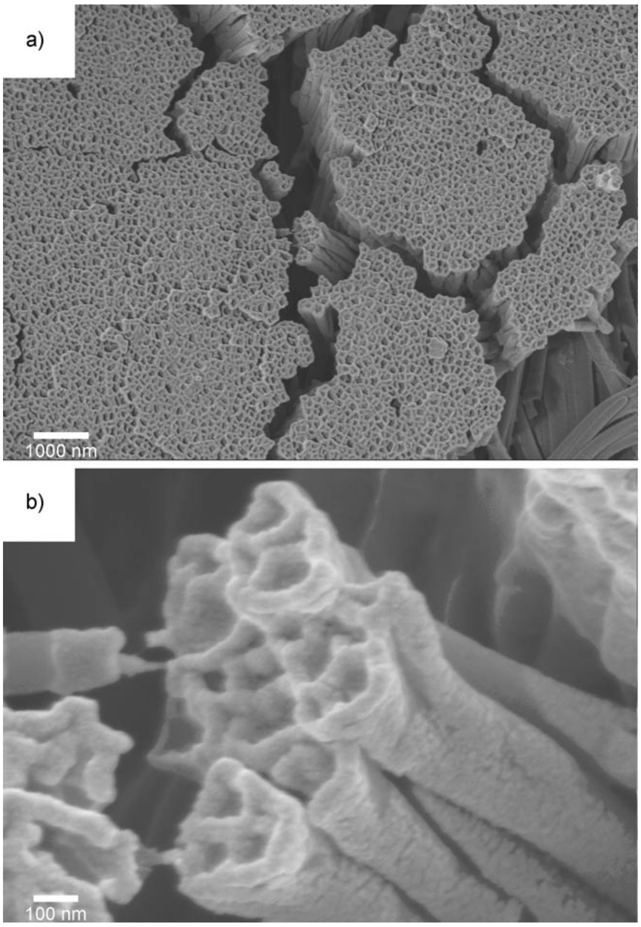

Figure 2. Typical scanning electron micrographs of the platinum/carbon MPCNTs, showing: a) the aligned tubes and b) the tubes at higher resolution.

particles supported on carbon black.[13] This finding differs from previous attempts to prepare metal nanoparticles on the surfaces of carbon nanotubes, which did not yield a narrow size distribution and highly dispersed particles because metal nanoparticles were preferably formed at the defect positions of the CNTs.[14] In contrast to the conventional CNTs, the wall of the MPCNTs is composed of an interconnected 3D network with pore sizes ranging from 5 to 20 nm, which supports the formation of the highly dispersed metal nanoparticles.[15] Energy-dispersive X-ray analysis (EDX) of the Pt/MPCNTs (see Figure S4 in the Supporting information) demonstrated that the tubes were constructed of carbon and platinum, with carbon as the main component. Quantitative evaluation obtained from thermogravimetric analysis (TGA) showed that the product contained approximately 30 wt% platinum (see Figure S5 in the supporting information). High-resolution TEM (HRTEM) images show small crystalline particles dispersed in the porous carbon matrix (Figure 3b). This finding proves that the current carbon structure effec-

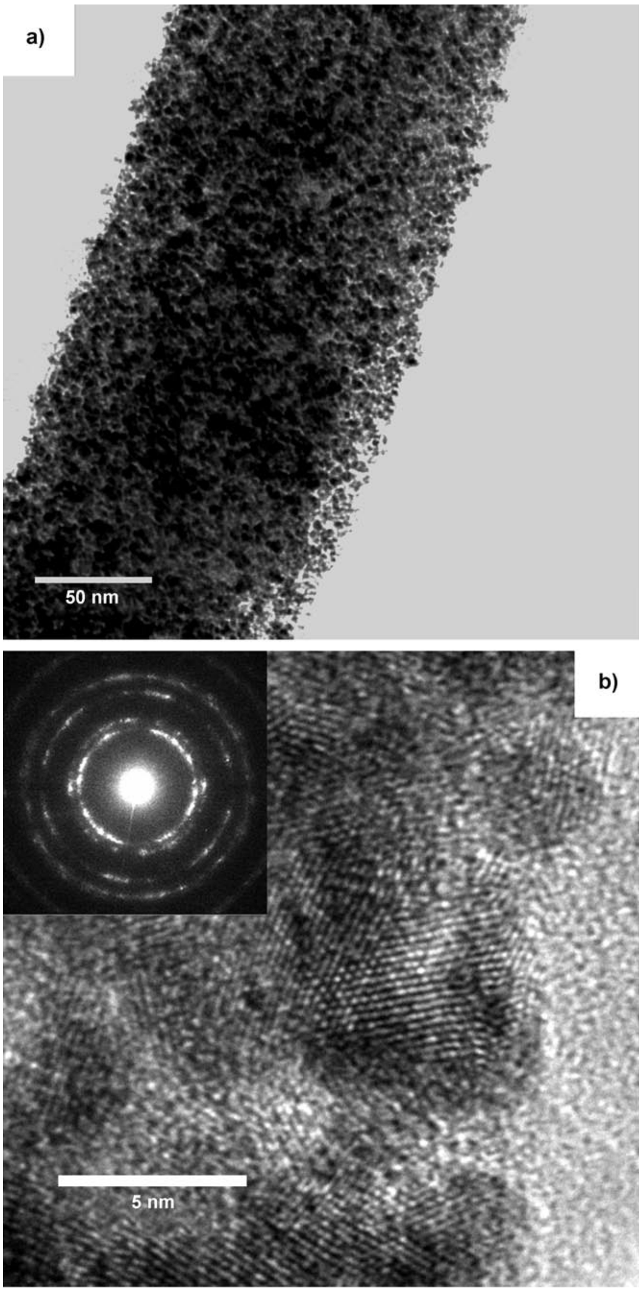

Figure 3. Typical TEM images of the platinum/carbon MPCNTs showing homogeneously dispersed platinum particles (a) and highly resolved platinum particles (b) in the carbon matrix. The SAED pattern (inset of b) shows the platinum nanoparticles are crystalline.

tively prevents particle agglomeration. It can be assumed that, because of the stability of the carbon matrix, this might also hold for longer operation times, thereby keeping the catalyst active and ensuring a long lifetime of the device. The crystallinity of the platinum nanoparticles was further proven by selected-area electron diffraction (SAED, Figure 3b, inset). It should be noted that the amount of platinum loaded into the pores of MPCNT was easily tuned by changing the concentration of the chloroplatinic acid solution (see Figure S6 in the Supporting information).

Analysis of nitrogen adsorption/desorption properties of the Pt/MPCNTs shows a type-IV isotherm with a pronounced hysteresis typical for mesoporous materials (Figure 4). The strong adsorption at lower pressures indicates the presence of a significant number of micropores and therefore only a fraction of the total Brunauer–Emmett–Teller (BET) surface area can be attributed to the mesopores. BET evaluation of the surface area of the Pt/MPCNTs revealed a specific surface area of 1171 $m^2 g^{-1}$. In comparison, the carbon supports for commercial platinum catalysts, such as the E-TEK catalyst, have a measured area of approximately 250 $m^2 g^{-1}$.[16] The Pt/MPCNTs containing interconnected micro- and mesoporous structures should not only provide more catalytically active sites, but also facilitate the transport of reactants and products during electrochemical reactions.[17]

In regards to electrode materials for fuel cells, an interconnected porous structure combined with a large surface area is essential for loading as many catalytically active platinum nanoparticles as possible and dispersing these particles homogeneously into the carbon matrix.[18] The electrocatalytic activities of the Pt/MPCNTs were tested by the oxygen electroreduction reaction (ORR). The ORR and its kinetic limitations are of fundamental interest from the viewpoint of fuel-cell applications: a solution of 0.5 M H_2SO_4 was completely saturated with oxygen by purging ultrapure oxygen for about 15 minutes with the Pt/MPCNT electrode.[19]

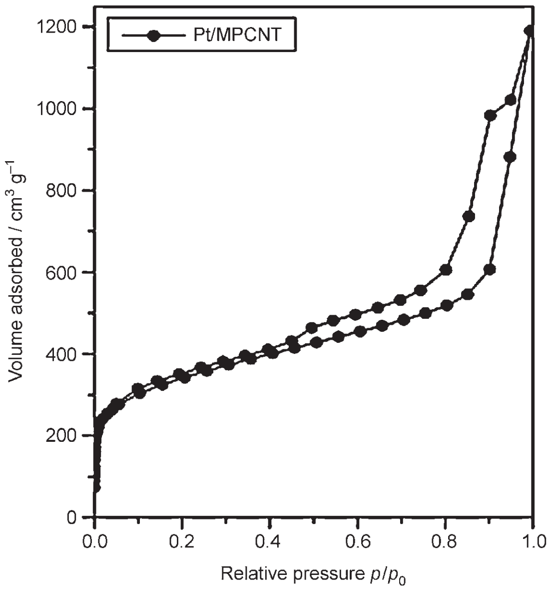

Figure 4. Nitrogen adsorption/desorption isotherms of mesoporous CNTs after loading with platinum nanoparticles.

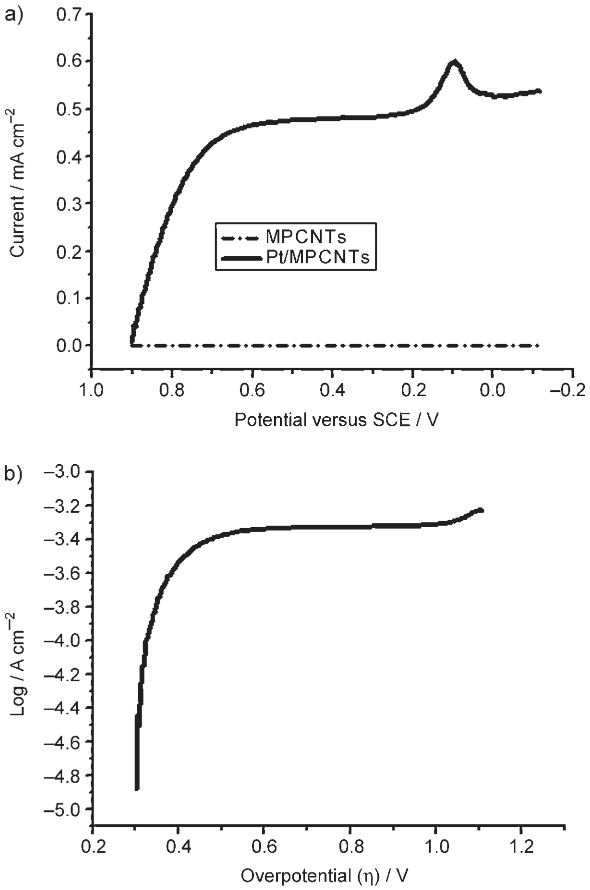

Figure 5. Linear voltammogram of the Pt/MPCNTs composite and MPCNTs (a) and the Tafel polarization curve of the composite for the ORR (b; 0.13 $mg\,cm^{-2}$ MPCNTs and 0.04 $mg\,cm^{-2}$ Pt). Solution: 0.5 M H_2SO_4, saturated with oxygen. Scan rate: 20 $mV\,s^{-1}$.

The anchoring of platinum nanoparticles on MPCNTs led to a pronounced enhancement of the cathodic current relative to that of pristine MPCNTs (Figure 5a). The peak current of Pt/MPCNTs increased linearly with the square root of the scanning rate (see Figure S7 in the Supporting Information), which suggests that the diffusion of oxygen to the electrode surface is a current-limited process. Tafel plots were obtained from the onset region of the linear part of the polarized curve by using the reduced form of the Butler–Volmer equation.[20] A plot of $\log I$ versus the overpotential (η) for the composite is shown in Figure 5b. An exchange current density (j_0) of $4.4\times10^{-4}\,A\,cm^{-2}$ was obtained by extrapolating the linear region for the Pt/MPCNTs composite to zero overpotential. This value is comparable to the j_0 value of a single-wall CNT ($6.3\times10^{-4}\,A\,cm^{-2}$) as an electrode,[4c] but significantly higher than the value of $1.09\times10^{-7}\,A\,cm^{-2}$ for a commercial catalyst such as platinum black.[21] This result suggests that the Pt/MPCNTs are excellent electrocatalysts for promoting the ORR. The high performance of the Pt/MPCNTs for the ORR is related to the interconnected mesoporous platinum/carbon system, where the electron and reactants can access readily all of the electrocatalytic sites. The narrow size distribution of the platinum nanoparticles has a significant effect on the kinetics of oxygen reduction.[22] These metal-incorporated carbon materials may also be useful for the construction of fuel-cell anodes that operate by direct oxidation of methanol, where high platinum loading is essential.[23]

In summary, 1D nanoscale carbon/platinum electrodes with surface areas higher than $1100\,\mathrm{m^2g}$ were prepared in a controlled fashion by the combination of a template method with electrochemical procedures. Small platinum nanoparticles with a narrow size distribution were homogeneously dispersed in the interconnected porous carbon matrix. Electrocatalytic characterization demonstrated that these Pt/MPCNTs have excellent catalytic activities in the ORR. The j_0 value is about 1000-fold higher than that of commercially available platinum black. This general method should also be suitable for a variety of metal species. The composites, as prepared, are promising candidates for the construction of miniaturized fuel cells and catalytic reactors.

Experimental Section

Anodic alumina membranes were obtained from Whatman International Ltd. The average pore size of the membrane was about 200 nm (SEM) and the thickness was 60 μm. MPCNTs were obtained by thermal treatment of AB_2-functionalized tetraphenylcyclopentadienones in the membrane at 250 °C for 5 h, then at 350 °C for 5 h, and finally at 700 °C for 5 h under nitrogen by using a procedure described elsewhere.[7a] A gold film (100 nm) was evaporated onto one side of the MPCNTs/alumina membrane as the conducting layer. The MPCNT-loaded membrane served as a working electrode and a platinum foil was chosen as a counterelectrode. Electrochemical modification of the MPCNTs was performed in an aqueous solution of H_2SO_4 (0.1M) in the presence of 4-nitrobenzenediazonium tetrafluoroborate (2.0 mM) by scanning between 1.1 and −0.3 V (versus SCE).[12] A heavier loading of platinum on carbon was obtained using a solution of chloroplatinic acid (0.001M) containing $LiClO_4$ (0.1M) as the supporting electrolyte and platinum foil as the counterelectrode. The template was removed by soaking the samples in an aqueous solution of NaOH (0.1M). The product was rinsed with water and dried under N_2 for further investigation. Electrochemical measurements were performed using an EG&G potentiostat/galvanostat Model 2273 instrument. A conventional cell with a three-electrode configuration was used throughout this study. All the potentials are referenced to a saturated calomel electrode (SCE) unless specially mentioned.

SEM (1530 Gemini by LEO) was employed to determine the structure of the composites, and the images were acquired at an electron voltage of 3.0 kV. The samples as prepared were dispersed in ethanol by sonication and transferred to copper grids coated with carbon for TEM characterizations (Tecnai F20).

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