Multiwalled Carbon Nanotubes Grown on Carbon Paper as Support for Pt-Based Electrocatalysts

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The unique properties and structure of carbon nanotubes suggest many potential applications in various areas including electrocatalysis. Several techniques, such as arc discharge or laser ablation, have been used to grow carbon nanotubes, but catalytic decomposition of carbon materials is thought to be the best method to obtain carbon nanotubes on a substrate. We utilized the electrically conducting properties of carbon paper substrates to design a gas phase thermal decomposition reactor, which Ohmically heats the catalytic sites (1,2). Recently, using this newly designed reactor, we reported the growth of multiwalled carbon nanotubes (MWCNTs) on carbon paper of the type used as a backing electrode for fuel cells (3).

PtRu alloy is currently the most popular catalyst used in polymer electrolyte fuel cells for the oxidation of H_2 in the presence of several tens of ppm of CO. It is also the preferred catalyst used for the oxidation of methanol in direct methanol fuel cells. Our idea of growing carbon nanotubes on fuel cell electrode backing was to use these composite substrates as supports for important electrocatalysts like PtRu. The possibility of depositing very small PtRu clusters on carbon nanotubes is demonstrated in this report. High-resolution transmission electron microscopy (HRTEM) and field-emission scanning electron microscopy (FE-SEM) were used to characterize the structure of the nanotubes.

MWCNTs have been synthesized on carbon paper at ~ 800°C from the decomposition of ethylene. Co-Ni catalyst particles were dispersed by a silane intermediate layer adsorbed onto the carbon fibers (3). Figure 1 shows a typical SEM image of nanotubes grown on a carbon fiber. It is evident that a high density of nanotubes embraces the carbon fiber. The tubes are quite straight and follow a tip growth mode. Prior to depositing the PtRu alloy clusters, different pre-treatments of the MWCNT/carbon paper composite have been employed in order to anchor the bimetallic particles on the tubes. The pre-treatments include (i) methanol immersion for 30 min, (ii) silane pyrolysis at 800°C under H_2 + Ar for 10 min, and (iii) immersion in concentrated H_2SO_4 + HNO_3 (50:50 vol) at 140°C for 5 min.

PtRu alloy deposits were carried out by immersing the MWCNT/carbon paper composite for 2 h in a solution containing 0.04 M $PtCl_2$, 0.04 M $RuCl_3$, 1 vol% of sulfonated silane, 6 vol% water and ethanol. The composite was then dried at room temperature and reduced in a flow of H_2 + Ar at 580°C for 15 min before its examination by HRTEM. A typical HRTEM image showing deposits of PtRu particles is illustrated in Figure 2. This tube has an outer diameter of nearly 25 nm with a hollow of about 13 nm. The walls of the tube consist of about 15 cylindrical graphene layers. Nanoparticles are clearly seen to decorate the MWCNTs and they are evenly distributed over the walls of the MWCNTs. These particles are only located on the external surface of the tubes because the tubes were not opened by the pre-treatment used, even the short immersion in concentrated H_2SO_4 + HNO_3. The particle size distribution is quite narrow, with an average size of less than 1.5 nm. This is smaller than what is usually reported.

The use of the resultant PtRu/Nanotube/carbon paper composite material as an electrode is presently under investigation.

References :

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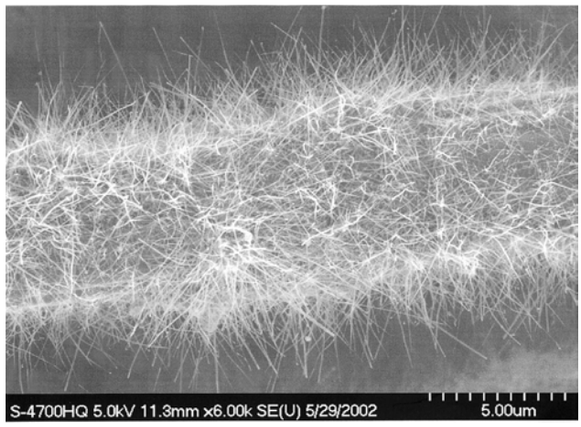

Fig.1 FE-SEM image showing carbon nanotubes grown on a carbon fiber

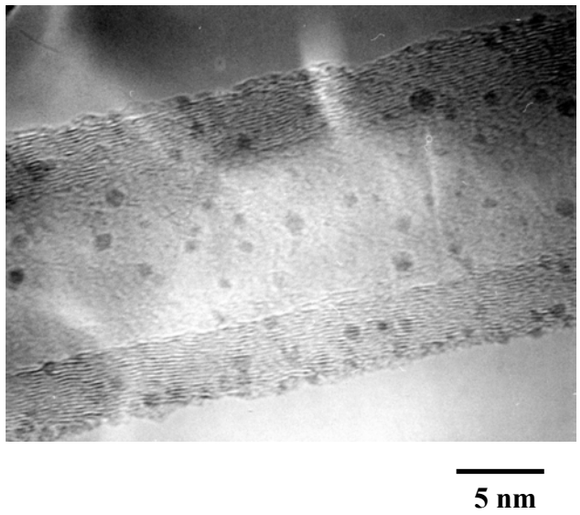

Fig.2 HRTEM image showing the size and distribution of PtRu particles deposited on a carbon nanotube