



Short communication

A study of different polyphosphazene-coated carbon nanotubes as a Pt–Co catalyst support for methanol oxidation fuel cell

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ABSTRACT

The composite of polyphosphazene-coated carbon nanotubes is prepared by a simple and efficient synthesis method and regarded as an improved catalyst support for direct methanol fuel cell. Catalyst of Pt–Co supported on polyphosphazene-coated carbon nanotubes is prepared using mixed reducing agents. The PZAF/MWCNTs, PZS/MWCNTs, Pt–Co/PZAF-MWCNTs and Pt–Co/PZS-MWCNTs are measured by transmission electron microscopy, X-ray diffraction and inductively coupled plasma. The electrocatalytic activity of Pt–Co/PZAF-MWCNTs, Pt–Co/PZS-MWCNTs catalysts for methanol oxidation has been investigated by cyclic voltammetry. The composite of Pt–Co/PZAF-MWCNTs shows a good distribution, small particle size and high mass activity.

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1. Introduction

Direct methanol fuel cells (DMFCs) have attracted much attention of researchers due to their high energy density, non-pollution and other great advantages. However, the commercialization of DMFCs is hampered by two major factors, which including the high cost of noble metal catalysts and the poisoning of the Pt electrode by CO [1–4]. Thus, many researchers have taken an effective approach to improve the catalytic activity as well as reduce the cost of the catalyst by using multi-component alloy catalysts. Recently, many researchers have developed Pt-based alloy catalysts with high activity for the ORR such as Pt–Ru, Pt–Pd, Pt–Co and Pt–Sn [5–9]. Besides, these Pt-based alloy catalysts have good tolerance to CO poisoning compared with pure Pt catalysts [10–12]. It has been found that Pt–Co alloys have high activity and excellent tolerance to CO poisoning in comparison with pure Pt catalysts [13–16], and Co is much cheaper than precious metal Ru. However, the synthesis of the composite has some defects like the complicated preparation of catalyst supports and the poor dispersion and distribution of Pt–Co particles.

On the other hand, carbon nanotubes (CNTs) exhibit excellent performance because CNTs possess unique structure and particular morphologies. Thus they have high specific surface area, corrosion resistance, good electronic conductivity and high stability [17,18]. Unfortunately, there are insufficient binding sites on CNTs for anchoring Pt alloy nanoparticles since CNTs are chemically inert. In addition, even some nanoparticles deposit on CNTs to agglomerate to a large particle, which will cause large particle size, poor dispersion and distribution. Therefore, making surface modification of CNTs is essential. The two main strategies of this process are covalent functionalization and noncovalent functionalization. Covalent functionalization of CNTs is usually carried out on the basis of harsh acid oxidation treatments mainly [19–22]. The oxidative step will lead to a loss of the novel properties of CNTs, such as high conductivity and remarkable mechanical properties. While anchoring groups were introduced to the noncovalent functionalization of CNTs without affecting the structure and electronic network of the tubes. Our group has reported that MWCNTs were successfully functionalized with a polymer coating of fluorinated cross-linked poly[cyclotriphosphazene-co-(4,4'-(hexafluoroisopropylidene)diphenol)] (PZAF) via noncovalent method [23]. The polyphosphazene-coated carbon nanotubes were used as Pt catalyst support, not only MWCNTs' characteristics were preserved, but as well achieved the result of having well-dispersed Pt nanoparticles, small particles size and high catalyst

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activity. As we just discussed above, Pt has two disadvantages of high cost and the poor tolerance to CO poisoning. And recently, efforts in electrocatalysis have focused on decreasing the Pt content by alloying Pt with less expensive metals. In this paper, we attempt to prepare PZAF-coated carbon nanotubes to support Pt–Co catalyst for methanol oxidation fuel cell. Another catalyst support was also prepared, that is: poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenol)(PZS) functionalized MWCNTs (PZS/MWCNTs).

2. Experiment

2.1. Materials

Hexachlorocyclotriphosphazene (HCCP, synthesized as described in the literature [24]) was recrystallized from dry hexane after sublimation (60 °C, 0.05 mmHg) twice before use. The melting point of the purified HCCP was 113–114 °C. 4,4'-(hexafluoroisopropylidene)diphenol (BPAF, purity > 99.5%) was purchased from Shanghai YiChao Chemical Co. Ltd. (Shanghai, China) and was used without further purification. 4,4'-sulfonyldiphenol (BPS, 99.8% purity) was obtained from Jiangsu Alonda High-Tech Industry Co. Ltd. (Jiangsu, China) and was used directly. Multi-wall carbon nanotubes (MWCNTs, with a diameter of 15–20 nm and a length of 5–15 μm) was obtained from Beijing CNano Technology Co. Ltd (Beijing, China). Chloroplatinic acid (AR), Cobalt chloride (AR), triethylamine (TEA, AR) and all the other reagents which have analytical reagent grade at least were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and were used directly.

2.2. Preparation of polyphosphazene-coated MWCNTs

In the preparation of PZAF/MWCNTs, we referred to our previous preparation method [23]. Firstly, 20 mg HCCP, 58 mg BPAF and 5 mg MWCNTs were dissolved in THF-absolute ethanol (the volume ratio of THF to absolute ethanol is 20:1 and then dispersed upon ultrasound (100 W, 40 kHz) for 10 min. The reaction began with the addition of 2 mL TEA into the dispersion above and was maintained in an ultrasonic bath (100 W, 40 kHz) at room temperature for 10 h. After polymerization, the precipitated product was isolated by centrifugation and was washed three times using ethanol and deionized water, respectively. Finally, put the above products into the oven and dried at 80 °C to obtain polyphosphazene-coated MWCNTs (PZAF/MWCNTs). Then prepare PZS/MWCNTs support with the similar method.

2.3. Preparation of Pt–Co/polyphosphazene-coated MWCNTs

Pt–Co/PZAF-MWCNTs catalyst in the nominal Pt: Co atomic ratio 3:1 was prepared using the following method. The synthesis of Pt–Co bimetallic nanoparticles on the functionalized CNTs was carried out by reducing Pt and Co salt precursors, namely, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. This reduction method refers to previous report [2]. 20 mg functionalized MWCNTs (PZS/MWCNTs or PZAF/MWCNTs) were added to 35 mL ethylene glycol (EG). The above mixture was sonicated for 30 min, and then was high-speed stirred for 1 h. Dissolved an aqueous solution containing 10.6 mg $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 1.6 mg $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ into 15 mL EG/5 mL H_2O . Then they were added into the mixture with vigorous stirring and reduced by slowly adding a reducing solution containing a mixture of 0.1 M NaBH_4 and 1.0 M NaOH. The mixture was quickly heated to 130 °C for 3 h to reduce the Pt–Co completely. Finally, the composites was filtered and washed with deionized water. Then they were dried at 100 °C in vacuum oven.

2.4. Structural characterization

The morphology and dispersion of the samples were observed using TEM (JEM-2100, JEOL), of which the accelerating voltage was 200 kV. Conduct crystal structure identification on a D/max-2200/PC X-ray diffractometer with a Cu/K α radiation source at a scanning rate of 5° s⁻¹ in the 2 θ ranging from 10° to 80°. Atomic absorption spectroscopy in inductively coupled plasma (ICP) was recorded on iCAP 6000 Radial.

2.5. Electrochemical measurement

The electrochemical investigations of the as-prepared Pt–Co catalysts supported on the functioned MWCNTs was measured using cyclic voltammetry (CV) at room temperature on a Autolab PG302 electrochemical working station. A standard three-electrode cell was employed with platinum foil as a counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode was fabricated by casting Nafion-impregnated catalyst ink onto a glassy carbon electrode. 2.0 mg composite was first ultrasonically dispersed into the mix of 0.5 mL of ethanol and 25 μL of ethanol containing Nafion solution (5 wt%, DuPont) for 30 min to form a catalyst ink. Then 10 μL catalyst ink was dropped onto the glassy carbon electrode and dried at room temperature. Methanol electro-oxidation experiments were performed at room temperature in 0.5 M H_2SO_4 and 0.5 M CH_3OH aqueous solution in the potential range of 0–1 V at a sweep rate of 10 mV s⁻¹.

3. Results and discussion

3.1. Structure and morphology characterization

From Fig. 1(a and b), it was clear that the nanocables were composites with a CNT core and amorphous polyphosphazene shell and the composites were prepared according to the hard template theory. As MWCNTs have a relatively high surface energy, the comonomers HCCP and BPAF can easily adhere to the surface of MWCNTs. During the reaction, there was a wonderful discovery that the thickness of the PZAF shell did not change any more even with the increasing amount of PZAF coating—that is the mass ratio of MWCNTs to comonomers HCCP and BPAF. In other words, when the comonomers exceeded the given concentration, thus another polymer phase was found and dissociated in the solution, and the diameter of the shell always kept 1 nm around—a very thin cover. This is because comonomers which had been adhered to the MWCNTs began to react as soon as TEA was added, and the excess comonomers dissociated in the solution also started to polymerize themselves. As a result, another polymer phase was found and the diameter always remained unchanged. However, PZS\MWCNTs can get much thicker coating of PZS shell using the same method and in the same concentration. It was confirmed in our previous study that the PZS shell was formed layer by layer on the surface of MWCNTs [25], but the formation of PZAF shell layer by layer cannot succeed on the surface of PZAF\MWCNTs. It is supposed that PZAF have bulky groups $-\text{CF}_3$, which suppress the shell layer formation. Fig. 1(c and d) display the nanoparticles are uniformly dispersed on the PZAF/MWCNTs surface and the average particle size is 2.5 nm, while the nanoparticles are randomly deposited on the PZS/MWCNTs surface and the particle size is bigger, even some particles tend to agglomerate and connect together. Our groups have been proved that the PZAF/MWCNTs could not only improve the dispersion of nanoparticles, but also obtain small particle size compared with pristine MWCNTs[23]. They believed that the fluorine on the PZAF/MWCNTs surface contributes to the improvement of nanoparticles deposition. From the structures of PZAF and PZS

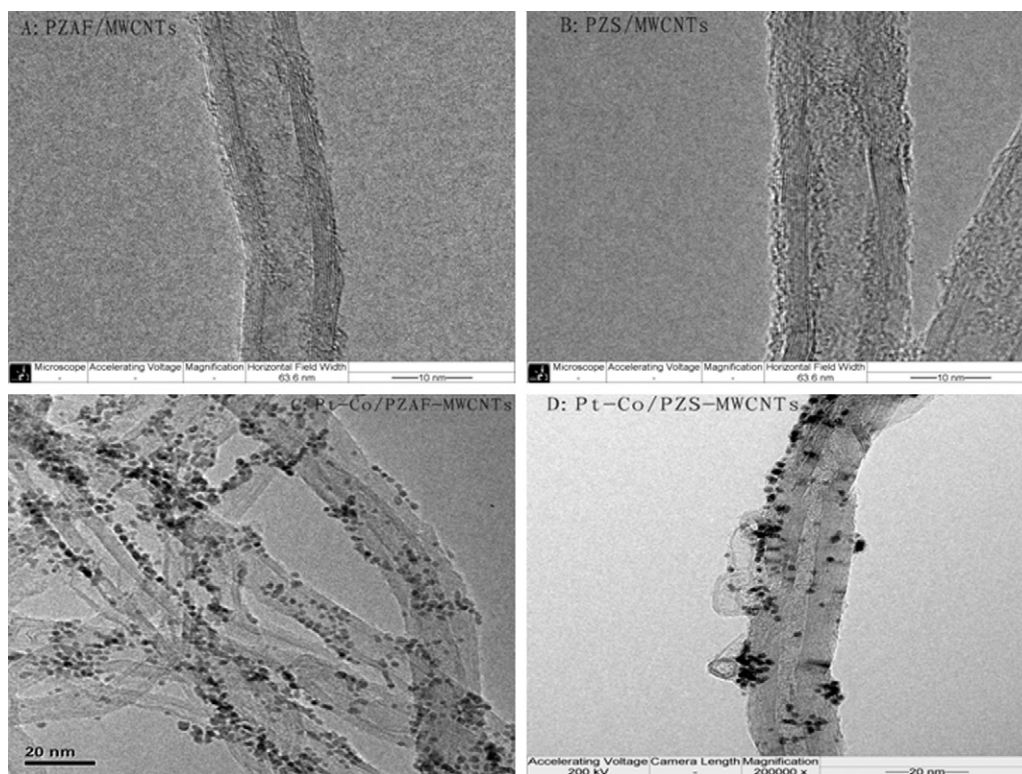


Fig. 1. The typical TEM images of polyphosphazene-coated MWCNTs, Pt-Co/PZAF-MWCNTs and Pt-Co/PZS-MWCNTs.

(see in Table 1), we can conclude that $-CF_3$ improve the better dispersion and obtain smaller particle size.

Crystallinities of the Pt-Co/PZAF-MWCNTs and Pt-Co/PZS-MWCNTs were investigated by XRD, and the results are shown in Fig. 2. The 2θ peaks at ca. 26° were signals from graphite-like CNTs. Generally, three peaks in the XRD pattern of Pt/PZAF-MWCNTs are characteristic of face-centered cubic (fcc) crystalline Pt metal, corresponding to the (111), (200) and (220) planes at 2θ values of 39.7° , 46.3° , 67.6° , respectively, while both the Pt-Co/PZAF-MWCNTs and Pt-Co/PZS-MWCNTs have a slight shift to higher Bragg angles, i.e., the peaks of Pt (111) that slightly shifted to 40° were observed both in the two composites. Besides, no individual peaks of Co were detected and the cobalt actually existed in the composite which can be confirmed by ICP (see next), which indicated the incorporation of Co atoms into Pt atoms. However, there is a big difference that the peaks of Pt-Co/PZAF-MWCNTs are

much broader than the peaks of Pt-Co/PZS-MWCNTs and the average particle size of the deposited Pt-Co catalysts were calculated to be 2.2 nm, 2.4 nm in terms of the Scherrer's equation, which are a little smaller than the result presented by TEM. XRD is mass sensitive, namely, a small fraction of larger particles within the samples would produce the narrower diffraction peaks [13]. Thus, the broad diffraction peaks suggests that the as-prepared Pt-Co alloys exist in small particle sizes with a narrow size distribution, which further confirmed that $-CF_3$ groups improve the better dispersion and obtain smaller particle size.

Table 2 shows the practical composition of as-prepared Pt-Co bimetallic catalysts using an ICP analysis. From the ICP analysis, the atomic ratio of Pt to Co is 5:1 (PZAF), 4:1 (PZS), respectively, which has a little deviation in comparison with the nominal atomic ratio. The loss of Co was believed to be caused by the hydrolysis of the salt precursor $CoCl_6 \cdot 6H_2O$. From the data, we can also conclude that PZAF-MWCNTs supports improve the utilization of the Pt-Co catalyst, which indirectly demonstrates the fluorine atom has a significant interaction with alloy catalysts.

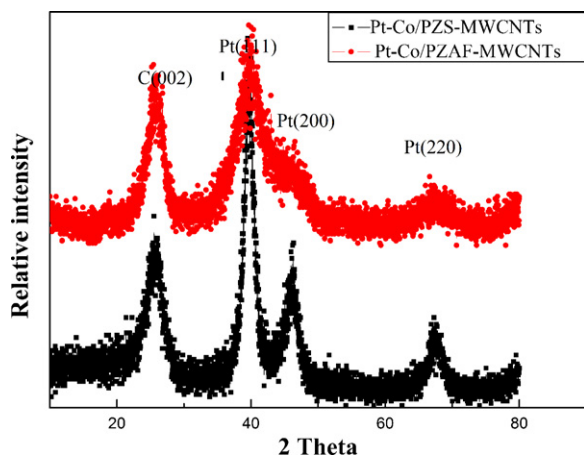
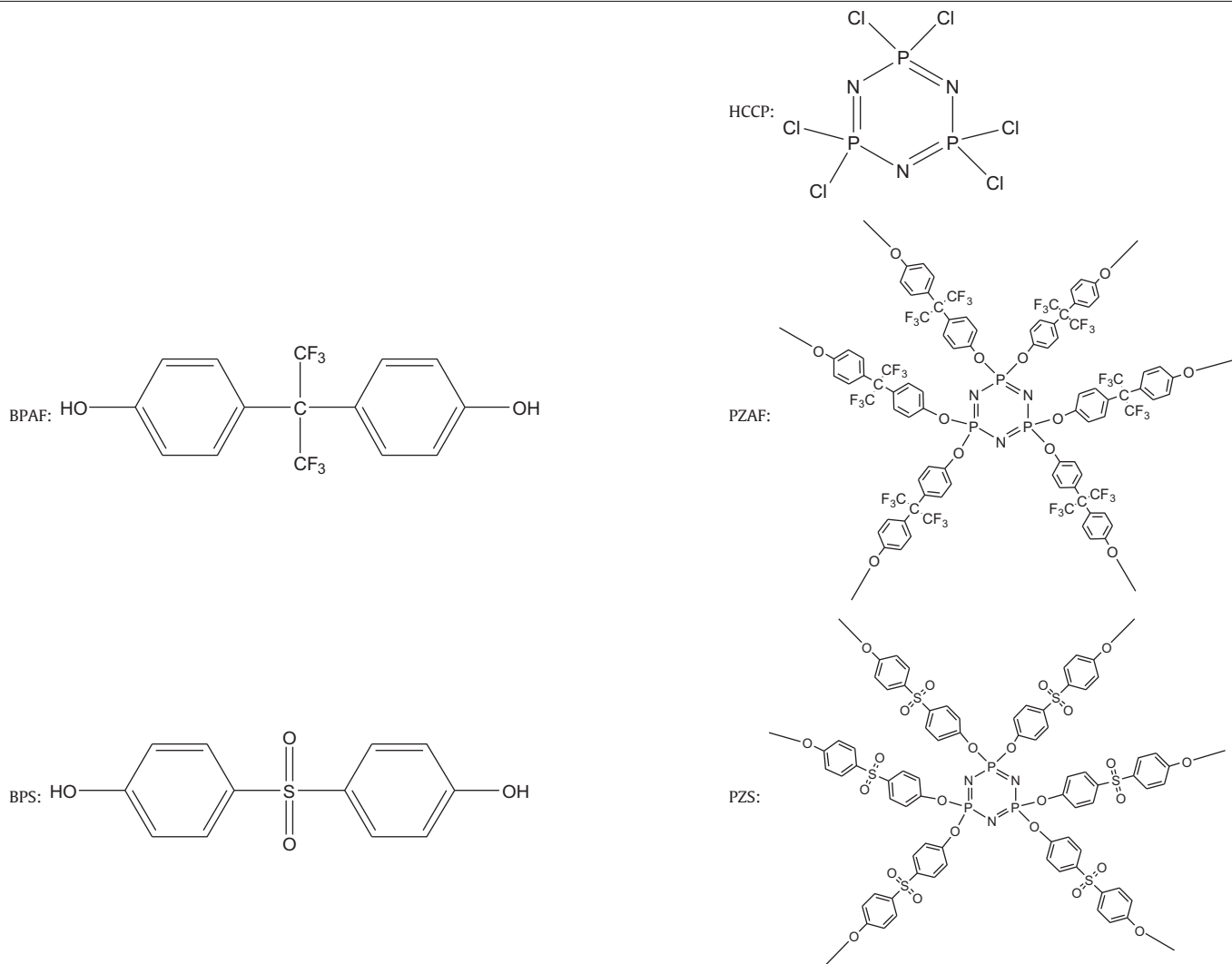


Fig. 2. XRD patterns of Pt-Co/PZAF-MWCNTs, Pt-Co/PZS-MWCNTs.

3.2. Electrochemical behavior

Fig. 3 shows the cyclic voltammograms (CVs) of 0.5 M CH_3OH in the 0.5 M H_2SO_4 solution at the Pt-Co/PZAF-MWCNTs, and Pt-Co/PZS-MWCNTs catalysts in the potential range of 0 V to 1 V at a sweep rate of $10 mV s^{-1}$. All electrochemical characteristic data of the tests are summarized in Table 3. It is observed that Pt-Co/PZAF-MWCNTs has a higher mass activity (MA) of about $231 mA mg^{-1} Pt$ at 0.58 V than the other catalysts. And the MA value of Pt-Co/PZAF-MWCNTs is also higher than the catalyst of Pt/PZAF-MWCNTs which was reported in our previous paper [23]. Such a high MA value is attributed to the corporation of Co atoms into Pt atoms. Moreover, it is good evidence that the PZAF-MWCNTs support with good dispersion of Pt-Co nanoparticles and small particle size can achieve better electrocatalytic performance than

Table 1
Structures of HCCP, BPAF, BPS, PZAF, PZS.



the PZS-MWCNTs support. Generally speaking, the I_f to I_b ratio is an index of the catalyst tolerance to the poisoning species. A higher ratio value indicates more effective removal of the poisoning species on the catalyst surface [21]. From the Table 3, we can know that the I_f to I_b ratio value of Pt-Co/PZS-MWCNTs is higher

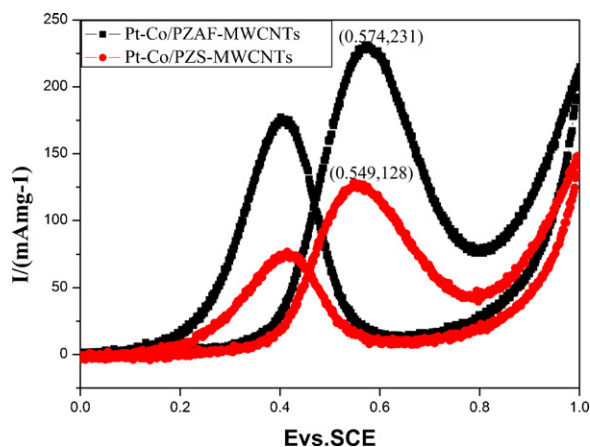


Fig. 3. Cyclic voltammogram of Pt-Co/PZAF-MWCNTs, Pt-Co/PZS-MWCNTs.

Table 2
Results of the quantitative analysis by ICP.

	Pt (%)	Co (%)
Pt-Co/PZAF-MWCNTs	10.23	0.5857
Pt-Co/PZS-MWCNTs	7.958	0.5237

Table 3
Results of the electronic catalyst by CV.

Samples	I_f/I_b	Mass activity (mA/mg Pt)
Pt-Co/PZAF-MWCNTs	1.305	231
Pt-Co/PZS-MWCNTs	1.707	128

than that of Pt-Co/PZAF-MWCNTs. It is believed that the poisoning effect depends greatly on the alloy composition. The percentage of Co atom with the atomic ratio of 4:1 (PZS) is higher than that of 5:1 (PZAF), which indicating that Co has an excellent tolerance to CO poisoning.

4. Conclusions

The composite of polyphosphazene-coated carbon nanotubes was prepared by a simple and efficient synthesis method. Pt-Co

alloy catalyst particles were reduced by ethylene glycol (EG) and a little amount of NaBH_4 . From the experience, we conclude that PZAF/MWCNTs are good catalyst support and Pt–Co particles on the surface of PZAF/MWCNTs display a great distribution and small particle size (2.2 nm). In addition, the composite of Pt–Co/PZAF-MWCNTs shows a high mass activity ($231 \text{ mA mg}^{-1} \text{ Pt}$) and excellent tolerance to CO poisoning. Moreover, the diameter of the polyphosphazene shell always kept 1 nm around— a very thin cover, which preserved the structure and electronic network of the tubes. The Pt–Co/PZAF-MWCNTs show great application potential in DMFCs.

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