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High aqueous solubility of carboxylated-carbon nanotubes as support for PtRu nanoparticles: Enhanced dispersion and electrocatalytic performance

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ABSTRACT

One great challenge in the development of noble metal nanoparticles (NPs)/carbon nanotubes nanohybrids as fuel cells electrocatalyst is to explore rationally functionalizing CNTs method for dispersion and stability of noble metal NPs catalysts with better electrocatalytic performance. Here we report a facile strategy to fabricate a carboxymethyl chitosan functionalized CNTs (CMC-CNTs) and demonstrate its application as a promising catalyst support material for direct methanol fuel cells. The developed route rationally utilizes the excellent water-solubility and abundant carboxyl (–COOH) functional groups of the CMC-CNTs as a superior supporting material for growing and supporting PtRu NPs. For methanol electrooxidation, the as-prepared PtRu NPs/CMC-CNTs nanohybrid has extremely large electrochemically active surface area (ESA) and exhibits better electrocatalytic activity and stability than PtRu NPs/CNTs catalyst. This provides a facile approach to synthesize CNTs-based nanoelectrocatalysts for high performance energy conversion devices in the future. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Due to their unique advantages, such as high power density and efficiency, relatively quick start-up, low operating temperatures, and the use of an easy-handling liquid fuel, direct methanol fuel cells (DMFCs) have been regarded as promising

candidates for future energy generation, which make them attractive for their application in portable electronic devices and transport [1–3]. Nevertheless, their performance is still limited by the poor kinetics of methanol oxidation at anode and the crossover of methanol from the anode to the cathode side through the proton exchange membrane. Moreover, high costs of the Pt-based electrocatalysts and susceptibility of the

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catalysts against poisoning of the CO-like intermediates formed during methanol oxidation are also the main obstacles to the commercialization of DMFCs [4–6]. One of the key factors in achieving high-energy densities and efficiency in DMFCs is the development of novel anode electrocatalyst, which is able to combine higher activity in methanol oxidation with enhanced tolerance for CO poisoning. At present, nanosized PtRu alloy supported on carbon black are widely used in DMFCs as anodic electrocatalysts that shows a significant amount of activity for methanol oxidation. Whereas Pt is well-known for its high activity as oxidation catalyst and, more particularly, the presence of Ru seems crucial and has been related to its ability to supply OH species at low potentials which contributes to the removal of poisoning CO species absorbed on the Pt by a bifunctional mechanism [4,6].

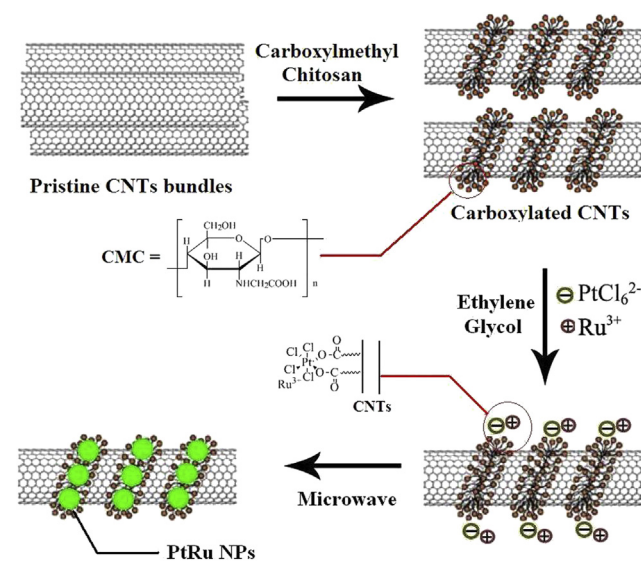
In order to further maximize the electrocatalytic performance of the Pt-based catalysts and minimize the usage of noble metals, a proper supporting material which can not only significantly enhance the availability of nanosized electrocatalyst surface area for electron transfer but also provide better transport of reactants to the catalyst is highly desirable [7–14]. Most recently, a variety of carbon support materials, such as carbon black [15–18], graphite nanofibers [19–21], carbon nanotubes [6,7,22,23], and graphene [24–26] have been intensively investigated for Pt-based electrocatalysts with enhanced electrochemical performance. In particular, due to CNTs' unique electronic and structural properties, such as high external surfaces, good electronic conductivity, large surface to volume ratio, and high chemical and electrochemical stability, the electrocatalytic activity and durability of PtRu NPs supported on CNTs were found to be better than that of the commercial PtRu/C [6,27,28].

Usually, supported metal NPs catalysts are often prepared by solution-phase processes and the key of this strategy is that the supports must have good dispersion in solvents without aggregation for a high accessible specific surface area, which is favorable for uniformly anchoring and growing small metal NPs. However, pristine CNTs are hydrophobic and have poor solubility in most solvents. More worsely, due to their insert graphitic surface and insufficient binding sites, it is difficult to deposit and grow uniformly distributed metal nanocrystals on pristine CNTs surface. To impart solution processability and functional groups to CNTs, surface functionalization of CNTs have been explored [10,29,30]. One of the most popular strategies is the use of strong oxidizing agent (e.g. HNO₃ or HNO₃/H₂SO₄ mixture) to introduce carboxyl (-COOH) or hydroxyl (-OH) functional groups on CNTs surface but it leads to lots of defects and loss their electronic conductivity and corrosion resistance [6,23,28]. Corrosion of carbon or CNT supports has been identified as one of the main reasons for the loss of the electrochemically active surface area (ESA) of Pt electrocatalysts and the reduced durability during fuel cell operations [8]. To preserve the advantageous structural and electronic properties of CNTs and introduce more binding sites, various of functional molecules [6,31], polymers [23,28] and surfactants [13] have been recently utilized to functionalize CNTs as supports for high performance catalysts, but rationally functionalizing CNTs as a superior support for significantly improved catalytic performance still remains a challenge.

In this paper, we demonstrate the use of carboxymethyl chitosan (CMC) to functionalize CNTs as a superior support to deposit small bimetallic PtRu NPs electrocatalysts with uniform distribution on CNTs. CMC is a biocompatible and biodegradable derivative of chitosan. Compared to chitosan, CMC has better water solubility and good ability to form films, fibers and hydrogels. For this reason, it has been extensively used in many biomedical fields such as a bactericide in wound dressing, artificial bone and skin, and as a component in drug delivery matrices [32,33]. With a flexible molecular backbone and lots of free carboxylic groups of CMC molecular chains can wrap itself helically around the CNTs, resulting in carboxylated-carbon nanotubes with high aqueous solubility. Then CMC acts as relative “soft” linkers between the CNTs and the precursors of metal ions or metal NPs (Scheme 1). The most important advantage is that, in contrast to the acid-oxidized CNTs, the CMC-functionalization treatment can not only produce carboxylic acid sites on the surface of CNTs for uniformly anchoring and growing the metal NPs catalyst, but also preserve the integrity and the electronic structure of CNTs. Therefore, the CMC modification is expected to eliminate aggregation of CNTs for high dispersion efficiency and its well-developed surface chemistries may direct growth of small metal NPs with uniform distribution on CNTs, and the obtained catalysts (PtRu NPs/CMC-CNTs) will show superb performance for the direct electrooxidation of methanol. As comparison, PtRu NPs were supported on the pristine CNTs and the electrocatalytic properties of PtRu NPs/CNTs catalysts for methanol oxidation were also investigated.

Experiment

Pristine multi-walled CNTs (length 5–15 μm, diameter 20–60 nm) were purchased from Shenzhen Nanotech Port Co. Ltd., China. Carboxymethyl chitosan was purchased from Alfa



Scheme 1 – Schematic diagram of the CMC-CNTs and preparation of PtRu NPs/CMC-CNTs nanohybrids.

Aesar. Except the specific statement, chemicals were of analytical grade and used as received.

The procedure for the noncovalent functionalization of CNTs with CMC (CMC-CNTs) is as follows: first, 100 mg of pristine CNTs was sonicated in 40 mL of water containing 20 mg of CMC at room temperature for 1 h and then the obtained solution was under vigorous stirring for 48 h. The above solution was centrifuged and washed with ethanol and water three times. The as functionalized CNTs were dried in a vacuum oven at 50 °C for 12 h and then the CMC-CNTs were obtained.

Deposition of PtRu NPs on the CMC-CNTs was carried out via microwave-assisted reduction process in ethylene glycol solution. The details were as follows: 20 mg of CMC-CNTs was mixed with 438 μL H_2PtCl_6 (38.6 mM) in ethylene glycol solution. After ultrasonication for 15 min, 350 μL RuCl_3 (48.2 mM) was added into above mixture and ultrasonic blended for 30 min. Then, the pH value of the solution was adjusted to 8–9 with 1.0 M KOH aqueous solution. The mixture was placed in a microwave oven and heated by microwave irradiation (800 W) for 10 min at 120 °C. The products were centrifuged and washed three times with distilled water. The obtained PtRu electrocatalysts supported on the CMC-CNTs, denoted as PtRu NPs/CMC-CNTs, were dried in vacuum oven at 60 °C for 12 h. For comparison, PtRu NPs supported on the pristine CNTs, labeled as PtRu NPs/CNTs, were prepared under the same procedure as described above.

Fourier transform infrared spectrometry (FTIR) (Nicolet, 6700) was employed to analyze the surface chemical compositions of the CMC-CNTs. The weight percentage of the CMC in the CMC-CNTs was determined by thermogravimetric analysis (TGA) (NETZSCH STA 409PC). The Raman spectrum (in Via, Renishaw, England) was also used to study the integrity and electronic structure of the samples. The metal Pt and Ru loading mass for the PtRu NPs/CMC-CNTs (or PtRu NPs/CNTs) catalyst was determined by Inductively Coupled Plasma-Atom Emission Spectroscopy (ICP-AES, Spectro Ciros). For electrochemical investigation, a glassy carbon (GC, 5 mm diameter) electrode was polished with the slurry of 0.5 and 0.03 μm alumina successively and washed ultrasonically in double-distilled water prior to use. The catalyst ink was prepared by dispersing 5 mg of catalyst in 5 mL of water by sonication. When a dark homogeneous dispersion was formed, a definite volume of the ink was dropped onto the GC electrode using micro-syringe. After dried in air, the electrode was coated with 10 μL of 0.05 wt.% Nafion ethanol solution to fix the catalyst powder. The electrochemical surface area (ESA) and the electrochemical performance of the electrocatalysts were evaluated by cyclic voltammetry. All electrochemical measurements were performed on a CHI660D electrochemical workstation (Chenhua Instrument Company of Shanghai, China). A conventional three-electrode glass cell was used with a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All the potentials reported herein were in respect to SCE. Double-distilled water was used throughout.

Results and discussion

Fig. 1 displays the FTIR spectra of CMC, pristine CNTs and CMC-CNTs. The FTIR spectrum for CMC (curve 3 in Fig. 1) when it is unattached to CNTs shows a typical profile with a

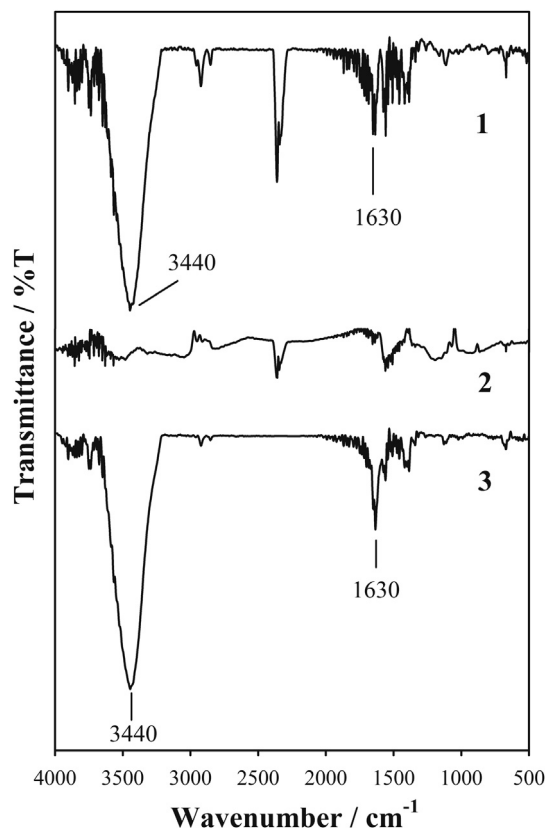


Fig. 1 – FTIR spectra of CMC-CNTs (1), pristine CNTs (2) and CMC (3).

very broad stretching bands $\nu(\text{O-H})$ at 3440 cm^{-1} and $\nu(\text{C=O})$ at 1630 cm^{-1} are assigned to the carboxyl groups of CMC. The pristine CNTs show typical absorption peaks of aromatic rings from 1600 cm^{-1} to 1450 cm^{-1} (curve 2 in Fig. 1). It is noted that the spectrum of the CMC-CNTs is very similar to that of CMC and all of the characteristic peaks of CMC are observed in the FTIR of CMC functionalized-CNTs (curve 1 in Fig. 1). In addition, an obvious absorption peaks at 2300 cm^{-1} in the spectrum of the CMC-CNTs ascribes to the IR absorption of CO_2 . Since the intensity of the characteristic absorption peaks in FTIR spectrum of CMC is very strong, the IR absorption peaks of CO_2 can not be observed. These results indicate that the CMC has been successfully wrapped onto the surface of CNTs.

We have also used TGA technique to examine the existence of CMC in CMC-CNTs nanohybrids. TGA was performed on a NETZSCH STA 409PC at a heating rate of 10 °C min^{-1} in N_2 atmosphere and the corresponding results are shown in Fig. 2. For the pristine CNTs, it exhibits excellent thermal stability and there is almost no weight loss in the measured temperature range of 400–800 K. However, for the CNTs with CMC modification, an obvious weight loss can be observed in the temperature range of 400–800 K, which should result from the decomposition of the surface-bound CMC. The TGA results further confirm that CMC is successfully coated onto CNTs. From the difference in weight loss of the CNTs without and with CMC at 800 K, it was estimated that about 9.8 wt.% of CMC was wrapped on the surface of functionalized CNTs.

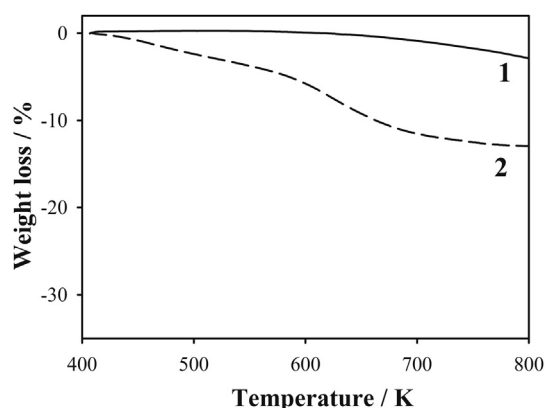


Fig. 2 – Thermal gravimetric analysis of pristine CNTs (1) and CMC-CNTs (2).

In addition, Raman spectroscopy is a powerful tool to characterize the extent of disorder or the degree of crystallinity in the functionalized CNTs. Usually, the peak at 1320 cm^{-1} should be assigned to the A_{1g} breathing mode of disorder graphite structure (i.e., the D band), and the peak at $\sim 1564\text{ cm}^{-1}$ assigned to the E_{2g} structure mode of graphite (i.e., the G band). The G band reflects the structure of the sp^2 hybridized carbon atoms. An additional side band at $\sim 1600\text{ cm}^{-1}$ was also observed, which is assigned as the D' band [6,28]. Both the D and the D' bands are due to the defect sites in the hexagonal framework of graphite materials. The extent of the defects in graphite materials can be quantified by the intensity ratio of the D to G bands (i.e., I_D/I_G) [6,23,28,31]. Fig. 3 shows that the value of the I_D/I_G ratio of CMC-CNTs is 1.42, which is slightly higher than that of the pristine CNTs (1.32). However, as reported previously [23], the value of I_D/I_G ratio of CNTs-AO (1.69) is much higher than that of the pristine CNTs, indicating that the harsh acid treatment causes significant structural damage of CNTs, which would lose the electronic conductivity and corrosion resistance of CNTs. The results from Fig. 3 imply that wrapping of CMC on the side-walls of CNTs can preserve the integral structure and electronic properties of CNTs and provides highly effective functional groups on the surface of CNTs for the subsequent deposition of the PtRu NPs.

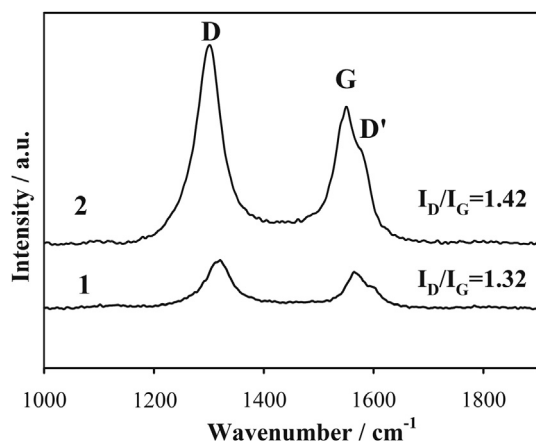


Fig. 3 – Raman spectrum of CMC-CNTs and pristine CNTs.

As mentioned in above, the excellent dispersibility in solvents is one of the key issues for CNTs as a superior support. Hence, a comparison of the dispersibility of CMC-CNTs and pristine CNTs in water was carried out. As shown in Fig. 4, CMC-CNTs can easily and uniformly disperse in water (Fig. 4b) and a dark, homogeneous CMC-CNTs aqueous solution was obtained after a short reaction time and could be stabilized for over 1 month without any visible precipitate. In contrast, it is difficult for pristine CNTs to uniformly disperse in water and the aggregation and precipitation are observed (Fig. 4a). This implies that the dispersibility of CNTs in water is greatly improved by the surface functionalization with CMC, which could be attributed to the aqueous solubility of carboxylic group as well as the intermolecular electrostatic repulsion, preventing aggregation of CNTs and induces stable CNTs suspension in water. The excellent dispersibility, sufficient binding sites and high accessible specific surface area of CMC-CNTs provide an excellent platform for construction of metal NPs/CNTs nanohybrids.

Fig. 5 shows the TEM images of the PtRu NPs/CMC-CNTs and PtRu NPs/CNTs nanohybrids. It can be seen from Fig. 5 that the CMC-CNTs are decorated successfully with lots of well-dispersed PtRu NPs. Their size distribution was evaluated statistically through measuring the diameter of 200 PtRu NPs in the selected TEM images. It is noted that the particle size of PtRu NPs distributes mainly between 2.0 nm and 5.5 nm with an average diameter of ca. 3.8 ± 0.5 nm. Notably, no NPs aggregation is clearly observed on the CNT surface. However, for the pristine CNTs, PtRu NPs do not disperse uniformly on the CNT surface and have a broad distribution (3.0–10.0 nm) with an average diameter of ca. 6.5 ± 1.5 nm. The reasons for this finding should be as follows. For the pristine CNTs without CMC modification, the defect sites generated during the growth and post-synthesis treatment of CNTs are usually not uniform. When PtRu NPs are deposited on the pristine CNTs,

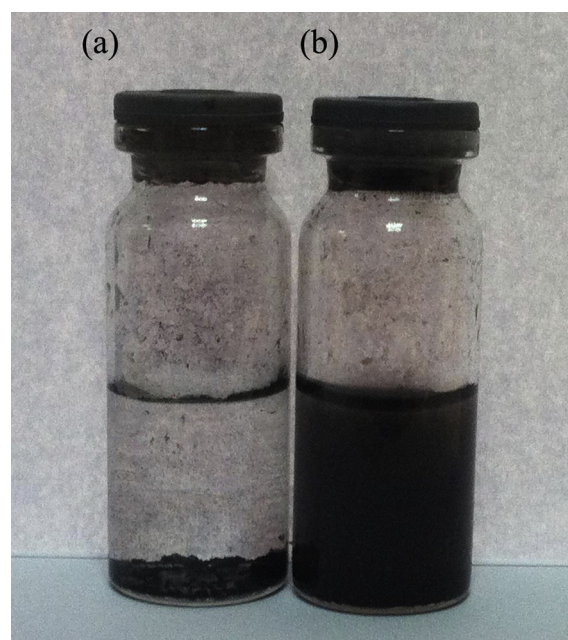


Fig. 4 – Digital photographs of 10 wt.% pristine CNTs (a) and CMC-CNTs (b) dispersed in water for one month.

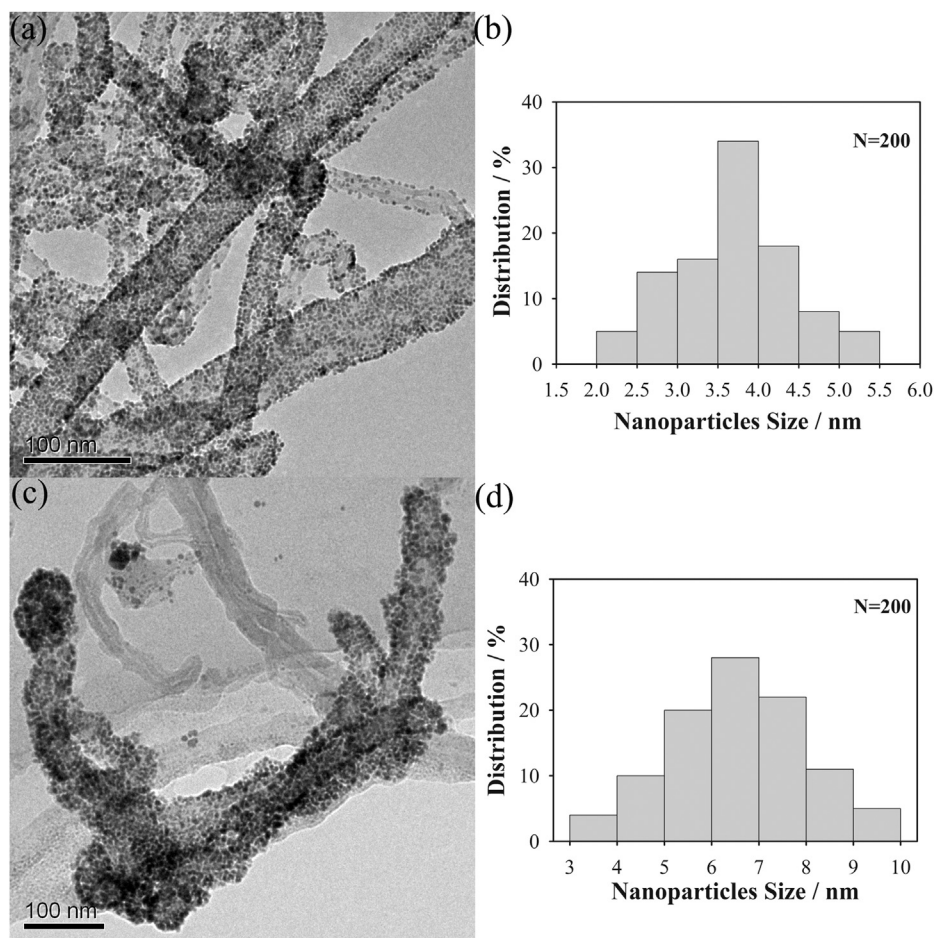


Fig. 5 – TEM images and size distribution of PtRu NPs of PtRu NPs/CMC-CNTs (a, b) and PtRu NPs/CNTs (c, d) nanohybrids.

PtRu NPs tend to deposit on these localized defect sites, thus leading to poor dispersion and aggregation. However, for the CNTs with CMC modification, the CMC layer on the surface of CNTs produces a uniform distribution of the carboxylic groups that serve as functional groups for the immobilization of Pt and Ru precursors on the surface of the CNTs through electrostatic interaction and coordination. Therefore, a much more uniform distribution of PtRu NPs is observed on the surface of the CMC-CNTs. The results of TEM indicate that CMC plays key roles in obtaining PtRu NPs with high dispersion and small particle size supported on the CNT surface. On the other hand, the composition of the prepared catalysts was determined by ICP-AES and the results show that there are 9.36 and 4.14 wt.% of Pt and Ru in PtRu NPs/CMC-CNTs, whereas PtRu NPs/CNTs have 8.85 and 2.60 wt.% of Pt and Ru. It is noted that the loading mass of the PtRu NPs supported on CMC-CNTs is higher than that on pristine CNTs, which confirms further that CMC-CNTs have high density and homogeneity of surface functional groups to anchor and grow metal NPs and are suitable support for electrocatalysts.

To demonstrate the capability of PtRu NPs/CMC-CNTs nanohybrids as a potential fuel cell electrocatalyst, the electrochemical performance was examined. Fig. 6 shows the cyclic voltammograms (CVs) of PtRu NPs/CMC-CNTs and PtRu NPs/CNTs nanohybrids measured in a nitrogen-saturated

0.5 M H₂SO₄ solution. Typical hydrogen and oxygen adsorption/desorption behaviors on platinum can be clearly observed on the two samples [23]. Based on the hydrogen adsorption-desorption charges, the ESA value of PtRu NPs supported on the CMC-CNTs or pristine CNTs can be calculated: [34]

$$\text{ESA} = Q_{\text{H}} / (0.21 \times [\text{Pt}])$$

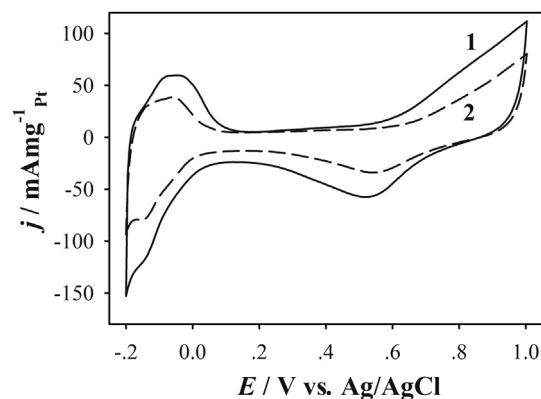


Fig. 6 – Cyclic voltammograms of PtRu NPs/CMC-CNTs (1) and PtRu NPs/CNTs (2) nanohybrids in nitrogen-saturated 0.5 M H₂SO₄ aqueous solution at a scan rate of 50 mV s⁻¹.

where Q_H (mC cm^{-2}) represents the mean value between the amounts of charge exchanged during the electro-adsorption and desorption of H_2 on Pt sites, $[\text{Pt}]$ is the Pt loading (mg cm^{-2}) on the electrode and 0.21 (mC cm^{-2}) represents the charge required to oxidize a monolayer of H_2 on bright Pt. Results show that the ESA value of the PtRu NPs/CMC-CNTs catalyst ($96.6 \text{ m}^2 \text{ g}^{-1} \text{ Pt}$) is 66% larger than that of PtRu NPs/CNTs catalyst ($58.2 \text{ m}^2 \text{ g}^{-1} \text{ Pt}$), which is attributed to the smaller particle size and much better dispersion of PtRu NPs on the CMC-CNTs. It is also noted that the ESA value of the PtRu NPs/CMC-CNTs catalyst is much more than that of E-TEK PtRu/C catalyst ($16.5 \text{ m}^2 \text{ g}^{-1} \text{ Pt}$) reported previously [6]. It is well known that the higher the ESA of a catalyst, the more electrochemical active sites would exist. The ESA results strongly imply that the PtRu NPs deposited on the CMC-CNTs are electrochemically more accessible, which is very important for electrochemical oxidation of methanol.

Finally the electro-catalytic activity of the PtRu NPs/CMC-CNTs as potential electrocatalysts for DMFCs was examined. Fig. 7 shows cyclic voltammograms (CVs) of PtRu NPs/CMC-CNTs and PtRu NPs/CNTs catalysts measured in nitrogen-saturated $0.5 \text{ M H}_2\text{SO}_4 + 1.0 \text{ M CH}_3\text{OH}$ aqueous solution. As shown in Fig. 7, the current exhibits the well-known features of methanol oxidation on PtRu electrocatalysts. As a kinetically controlled reaction, the activity of methanol oxidation on PtRu can be represented by the magnitude of the anodic peak. The higher anodic current indicates a higher electro-catalytic activity on PtRu NPs/CMC-CNTs, in agreement with the observation of a larger electrochemically active surface area. It is noted that the forward peak current of methanol oxidation on the PtRu NPs/CMC-CNTs catalyst is 546.9 mA mg^{-1} , being 1.9 and 5.6 times higher than that on the PtRu NPs/CNTs catalyst (276.4 mA mg^{-1}) and E-TEK PtRu/C catalyst (98.3 mA mg^{-1}) reported previously [6], respectively. On the other hand, when the catalyst support is changed from pristine CNTs to CMC-CNTs, the onset potential and forward peak potential of methanol oxidation shift more than 110 and 40 mV in negative direction, respectively. These show a noticeable feature that PtRu NPs/CMC-CNTs catalyst exhibits better electrocatalytic performance for methanol oxidation than PtRu NPs/CNTs catalyst, which are derived from PtRu

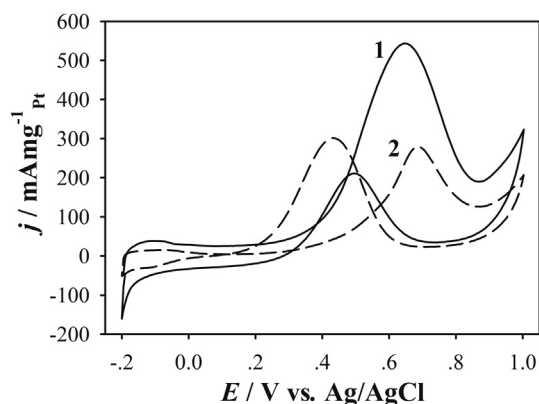


Fig. 7 – Cyclic voltammograms of PtRu NPs/CMC-CNTs (1) and PtRu NPs/CNTs (2) nanohybrids in nitrogen-saturated $0.5 \text{ M H}_2\text{SO}_4 + 1.0 \text{ M CH}_3\text{OH}$ aqueous solution at a scan rate of 50 mV s^{-1} .

NPs/CMC-CNTs nanohybrids having the following superior features over the PtRu NPs/CNTs sample: smaller sizes, better dispersion and higher electrochemical surface area of PtRu NPs on the CNT surface.

Fig. 8 shows the amperometric $i-t$ curves for PtRu NPs/CMC-CNTs and PtRu NPs/CNTs catalysts at a potential of 0.50 V in a nitrogen-saturated $0.5 \text{ M H}_2\text{SO}_4 + 1.0 \text{ M CH}_3\text{OH}$ aqueous solution for 30 min. Before each experiment was performed, the electrolyte was deaerated with N_2 for 15 min. These curves reflect the activity and stability of the two catalysts in catalyzing the methanol oxidation reaction. In the initial period, the decay current density decreased rapidly for all the catalysts. It may be due to the formation of the intermediate species (such as CO_{ads}) during the methanol oxidation reaction. However, during the whole time, the current density of methanol oxidation on PtRu NPs/CMC-CNTs is higher and the current density decay is much slower than that of PtRu NPs/CNTs catalysts, though the current decay with time was observed for the two catalyst modified electrodes. The PtRu NPs/CMC-CNTs catalysts retain a current density of 77.2 mA mg^{-1} at 1800 s, which is much higher than that of PtRu NPs/CNTs catalyst (2.86 mA mg^{-1}) and E-TEK PtRu/C catalyst (6.50 mA mg^{-1}) reported previously [35], respectively, indicating that PtRu NPs/CMC-CNTs catalyst is more suitable for long-term operation. Five repetitive measurements on PtRu NPs/CMC-CNTs catalyst gave a standard deviation of 6.8%, showing good reproducibility of the catalyst. Moreover, long-term cycle stability of the catalyst for methanol oxidation is a very important parameter in practical application. For PtRu NPs/CMC-CNTs, its peak current density approached 532 mA mg^{-1} at the first cycle and slightly decreased down to 460 mA mg^{-1} after 500 cycles without obvious change for forward peak potential (see the Supporting Information, Fig. S1). The increased stability also indicates that the anchor of PtRu on CNTs via CMC as interlinkers is strong. Furthermore, the use of CMC for modification of the CNTs which preserved their reservation of the structural integrity and high corrosion resistance increases the durability of PtRu NPs/CMC-CNTs electrocatalyst. These results in this study demonstrate the promising potential of noncovalent functionalization of CNTs by CMC as highly efficient and effective

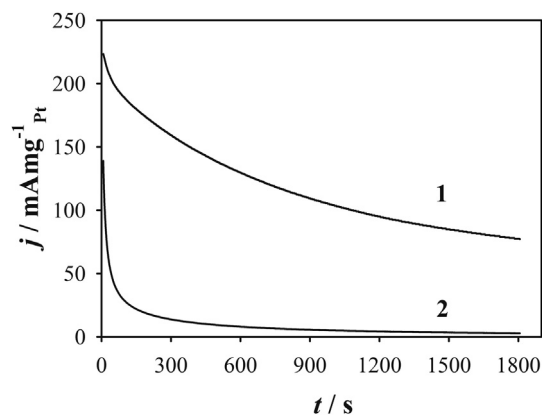


Fig. 8 – Amperometric $i-t$ test of PtRu NPs/CMC-CNTs (1) and PtRu NPs/CNTs (2) nanohybrids in nitrogen-saturated $0.5 \text{ M H}_2\text{SO}_4 + 1.0 \text{ M CH}_3\text{OH}$ aqueous solution at 0.5 V .

catalyst supports, especially for the development of PtRu electrocatalysts with high loading for the methanol electro-oxidation in DMFCs.

Conclusions

In summary, we have successfully developed a new strategy for the synthesis of noble metal NPs/CNTs nanohybrids based on the CMC-functionalized CNTs. Thanks to the excellent dispersion of CMC-CNTs in water and its much higher density and homogeneity of surface functionalization groups, small PtRu NPs with an average diameter of ca. 3.8 ± 0.5 nm were uniformly deposited on CNTs surface. Most importantly, compared to PtRu NPs/CNTs nanohybrids, PtRu NPs/CMC-CNTs nanohybrids toward methanol electrooxidation exhibit significantly enhanced catalytic current density, lower oxidation peak potential, and longer-term operation stability, due to the smaller particle size and higher dispersion of PtRu NPs on CMC-CNTs, higher electrochemical surface area and the structural integrity of CMC-CNTs. The developed CMC-CNTs should be the promising catalyst support for noble metal NPs in fuel cells.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.ijhydene.2014.03.022>.

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