Indian Journal of Chemistry
Vol. 58A, October 2019, pp. 1103-1108

Carboxymethylcellulose sodium-assisted uniform dispersion of PtRu nanoparticles on carbon nanotubes towards enhanced electrocatalytic oxidation of methanol

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Received 10 August 2018; revised and accepted 24 September 2019

Carbon nanotubes (CNTs) have been ideal catalyst support because of their high conductivity, chemical stability, and large specific surface area, but their inert surface have not been offer efficient groups for the anchoring of noble metal nanoparticles (NPs). Here, we present a general approach for the preparation of noble metal NPs/CNTs catalysts in a water-ethylene glycol system using carboxymethylcellulose sodium (CMS) as link. The functionalization of CNTs by CMS has been simple and can be carried out at room temperature, and the PtRu NPs have been uniformly anchored on CNTs with no formation of aggregates. Cyclic voltammetry study indicates that the resulting catalysts (PtRu NPs/CMS-CNTs) showed superb performance for the direct electro-oxidation of methanol, which can be ascribed to the constructing "ideal" triple-phase boundary structure at the interface between PtRu NPs, CMS and CNTs. This work may also demonstrate a gentle approach to fabricate robust catalysts with metal nanocrystaline on CNTs for broad applications in energy conversion devices in the future.

Keywords: Carbon nanotubes, Carboxymethylcellulose sodium, PtRu nanoparticles, Electrocatalyst, Methanol electrooxidation

Due to their high-energy conversion efficiency, low operating temperature, and environmental friendly nature, direct methanol fuel cells (DMFCs) have received increasing attention as clean power sources in electric vehicles and electronic portable devices[1]. For DMFCs, one of the key materials is effective electrocatalysts with low over potentials for methanol oxidation reaction (MOR) at anode electrode. Currently, platinum and ruthenium alloyed nanoparticles (PtRu NPs) supported on carbon black (PtRu NPs/C) is the most widely used catalyst[2] in DMFCs. However, during fuel cell operation, the PtRu NPs/C catalyst is continuously exposed to harsh electrochemical conditions, such as strong acidic medium and high electrode potentials, thereby seriously corroding the carbon black support. As a result, the PtRu NPs can easily detach from the carbon black support, thereby largely diminishing the overall catalytic surface and also resulting in poor long-term stability.

To overcome these problems, it is highly desirable to use other more durable materials, e.g., carbon nanotubes (CNTs)[3], graphite nanofibers[4] and graphene[5] as the catalyst support. Amongst, CNTs are ideal catalyst support, owing to their large surface area, excellent conductivity, outstanding chemical stability and high mechanical strength[6]. Over the past few decades, many research groups reported a variety of metal NPs/CNTs electrocatalysts for promoting the activity of MOR. Inherently, pristine CNTs are chemically inert, so that deposition of uniformly distributed metal nanocrystals on CNTs intensively relies on the activation of their graphitic surface. To this end, CNTs can be treated by harsh oxidative acids to generate anchoring carboxyl groups. However, the acidic oxidation process has the risk to create abundant defects, thereby greatly decreasing the conductivity of the CNTs, as well as their resistance against corrosion. Alternatively, CNTs can be modified with functional polymers, such as poly(diallyldimethylammonium chloride)[7], poly(allylamine hydrochloride)[8], poly(vinylpyrrolidone)[9], 1- aminopyrene[10] and benzyl mercaptan[11], which can wrap the CNTs via noncovalent interaction (e.g., π–π stacking and/or hydrophobic interaction). Compared with acidic oxidation process, this gentle surface functionalization process can generate dense, homogenously distributed anchoring groups on the CNTs without diminishing the conductivity of the CNTs. Despite these advantages, most of these functional polymers used are nonconductive, which could passivate the surface of the metal NPs, making their active sites inaccessible. Furthermore, functionalization of the CNTs with nonconductive polymers does not allow the construction of "ideal" conductive triple-phase boundary structure[12] at the interfaces among metal NPs, polymer and CNTs, thereby not fully utilizing the overall electrocatalytic performance of the metal NPs/CNTs catalyst because of the existence of the conduction barrier.

Herein, we report the preparation of highly dispersed PtRu NPs on CNTs using conductive CMS as the surface linker for MOR (Scheme 1). The CMS can provide abundant highly distributed anchoring groups (e.g., $-COO^-$ groups) to the CNTs, allowing stronger adsorption of the Pt and Ru precursor ions (i.e., $PtCl_6^{2-}$ and Ru^{3+}) and anchoring of the PtRu NPs reduced. Moreover, CMS is an anionic polymer electrolytes, which not only can increase the ionic conductivity of the catalytic layer but also can create the preferred "ideal" conductive TPBs structure at the interface. With these unique characteristics, the as-prepared PtRu NP/CMS-CNT electrocatalysts may show high performance for MOR.

Experimental

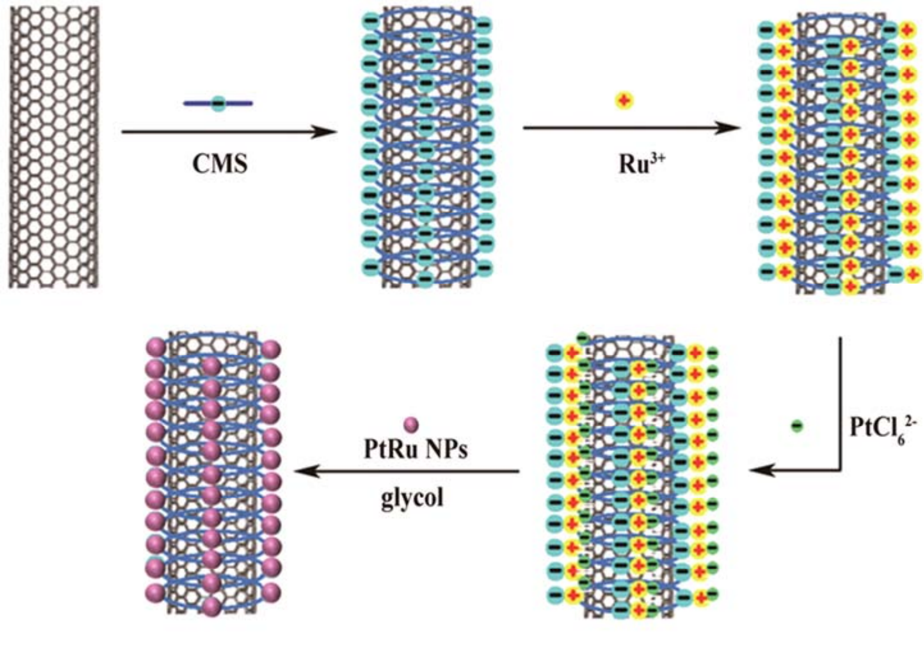
Materials

Pristine multi-walled CNTs (length, 5–15 mm; diameter, 20–60 nm) and CMS were purchased from Shenzhen Nanotech Port Co. Ltd., (Shenzhen, China) and Alfa Aesar (Ward Hill, USA) respectively. All other materials (analytical grade) were purchased from domestic supplies and were used as received without further purification.

Preparation of PtRu NPs/CMS-CNTs electrocatalysts

The preparation of PtRu NPs/CMS-CNTs involved functionalization of CNTs with CMS and subsequent deposition of alloyed PtRu NPs on the CMS-CNTs. Briefly, pristine CNTs (100 mg) were dispersed by sonication in a mixture of ethanol (4 mL), water (6 mL) and CMS (20 mg) at room temperature for 48 h, followed by vigorous stirring for 1 day. The resultant CMS-functionalized CNTs were filtered out from the above mixture using a nylon 66 membrane (0.22 µm) and washed three times with water, followed by drying in a vacuum oven at 50 °C for 12 h.

To deposit PtRu NPs, CMS-CNTs (20 mg), H_2PtCl_6 (19.3 mM, 875 µL), and $RuCl_3$ (24.1 mM, 710 µL) was mixed in the mixture of ethylene glycol (8 mL) and water (12 mL) by sonication for 30 min.



Schematic showing the synthesis route of the PtRu/CMS-CNTs electrocatalysts.
Scheme 1

Then, the pH value of the mixture was adjusted to 8–9 with 1.0 M KOH solution, followed by sonication for another 5 min. Finally, the mixture was heated by microwave irradiation (800 W) at 120 °C for 10 min. The resultant PtRu /CMS-CNTs catalyst were collected by centrifugation, washed three times with water, and then dried in a vacuum oven at 60 °C for 12 h. For comparison, PtRu NPs supported on the pristine CNTs (PtRu NPs/CNTs) were prepared under the same procedure as described above.

Characterization and electrochemical behaviors of the PtRu /CMS-CNTs electrocatalysts

Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy were carried out on an IR Tracer-100 spectrophotometer (Shimadzu, Japan) and a LabRam-010 confocal Raman spectrometer (Horiba, France), respectively. Transmission electron microscopy (TEM) images were obtained on a JEM-2100 F microscope (JEOL, Japan). The loading amount of PtRu NPs on PtRu/CMS-CNTs and PtRu/CNTs electrocatalysts were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES, IRIS-1000, USA). All electrochemical measurements were performed on a CHI660D electrochemical work station (CHI Instrument Company, Shanghai, China). Doubly distilled water was used throughout all the experiments.

Electrochemical measurements were performed in a conventional three-electrode electrochemical cell, using a platinum wire and a Reversible Hydrogen Electrode (RHE) as the counter electrode and the reference electrode, respectively. All the potentials were quoted versus RHE. The working electrode was prepared by loading electrocatalysts on a glassy carbon (GC, 5 mm in diameter) electrode. Before use, the GC electrode was sequentially polished with the slurry of 0.5 and 0.03 μm alumina powders to give a mirror-like surface finish. Then, the catalyst ink (20 μL), prepared by dispersing of catalyst (4 mg) in water (4 mL), was dropped onto the GC electrode and dried in air. Finally, ethanoic Nafion solution (0.05 wt.%, 10 μL) was dropped onto electrode surface to fix the catalyst powder.

Results and Discussion

The PtRu /CMS-CNTs electrocatalysts was prepared using CMS as the surface linker. The FTIR spectra of CMS, pristine CNTs, and CMS-CNTs are shown in Fig. 1. For CMS, the 1328 and 3440 cm^{-1} bands are assigned to the bending vibration and stretching vibration of the OH group respectively, while the 1635 and 1418 cm^{-1} bands are assigned to the asymmetric vibration and symmetric vibration of the C=O group, respectively. The band at 1052 cm^{-1} is assigned to the symmetric stretching bands of the C-O-C group. For pristine CNTs, the bands ranging from 1600 to 1450 cm^{-1} are typical absorption peaks from its aromatic rings. Upon surface functionalization of the CNTs, the bands from CMS are clearly discerned on the spectrum of CMS-CNTs. To reveal the impact of CMS on the CNTs, we have further performed Raman spectroscopy studies. The Raman spectra for pristine CNTs and CMS-CNTs are shown in Fig. 2. The spectra both exhibit two strong bands at 1320 and 1572 cm^{-1}, which are assigned the D band and the G band of CNTs, respectively[13]. For pristine CNTs, its relative I_D/I_G intensity is 0.62, consistent with that reported previously[14]. Upon surface functionalization with

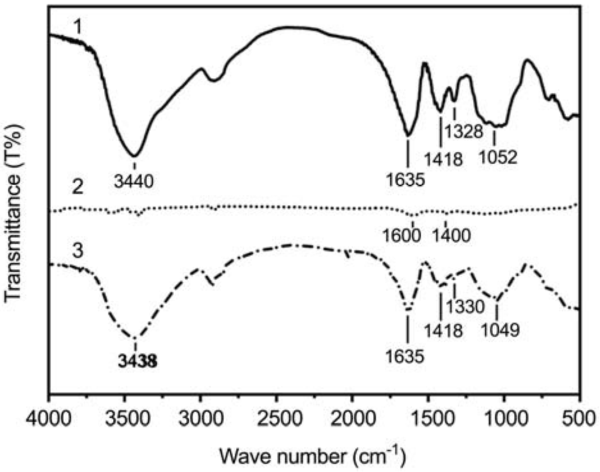


Fig. 1 — FTIR spectra of CMS (1), CNTs (2), and CMS-CNTs (3).

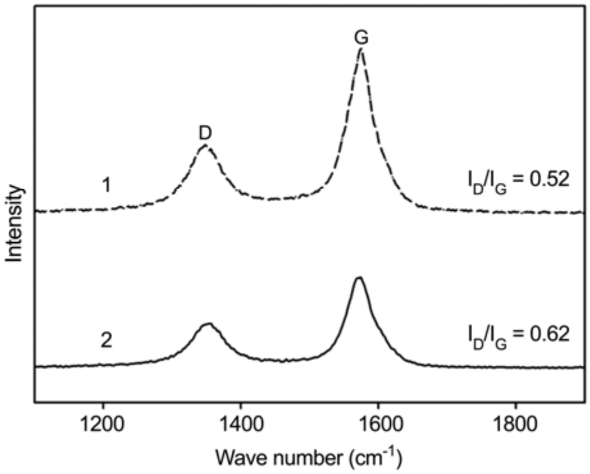


Fig. 2 — Raman spectra of CMS-CNTs (1) and CNTs (2).

CMS, the relative I_D/I_G intensity decreases from 0.62 to 0.52, further indicating the wrapping of the CMS on the side walls of the CNTs. The CMS-functionalized CNTs, thus, can offer abundant uniformly distributed anchoring sites (i.e., carboxyl groups and C=O groups), which can greatly promote the immobilization and dispersion of Pt and Ru precursors and subsequent PtRu NPs reduced, as confirmed by looking the TEM images. The TEM images of the PtRu/CMS-CNTs and PtRu/CNTs electrocatalysts are shown in Fig. 3. Clearly, small PtRu NPs were well dispersed on the CMS-CNTs, without aggregated particles observed. Their average particle size is ca. 3.5 ± 0.5 nm, determined by counting about 100 NPs. In contrast, the PtRu NPs on the PtRu/CNTs electrocatalysts aggregate to some extent, exhibiting relatively broad distribution with an average diameter of ca. 6.0 ± 1.0 nm.

To qualitatively evaluate the activity of the PtRu/CMS-CNTs electrocatalysts for MOR, we first calculated it's electrochemical surface area (ESA)[15]. The cyclic voltammograms (CVs) for the PtRu/CMS-CNTs and PtRu/CNTs electrocatalysts in a N_2-saturated 0.5 M H_2SO_4 solution is shown in Fig. 4. From the CV curves, the ESA of the PtRu NPs can be calculated using the following formula[16].

$ESA = Q_H / (0.21\times[Pt])$

Where Q_H (mC cm^{-2}) and [Pt] are the overall charge associated with electroabsorption of H on Pt surface and the loading amount of Pt(mg cm^{-2}) calculated from the ICP-AES results (Table 1). 0.21 mC cm^{-2} is the charge required to oxidize a

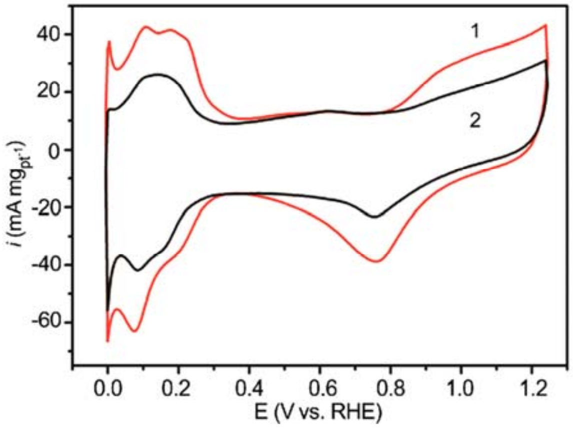


Fig. 4 — CV curves of PtRu/CMS-CNTs (1) and PtRu/CNTs (2) electrocatalysts in N_2-saturated solution of 0.5 M H_2SO_4 solution at a scan rate of 50 mVs^{-1}.

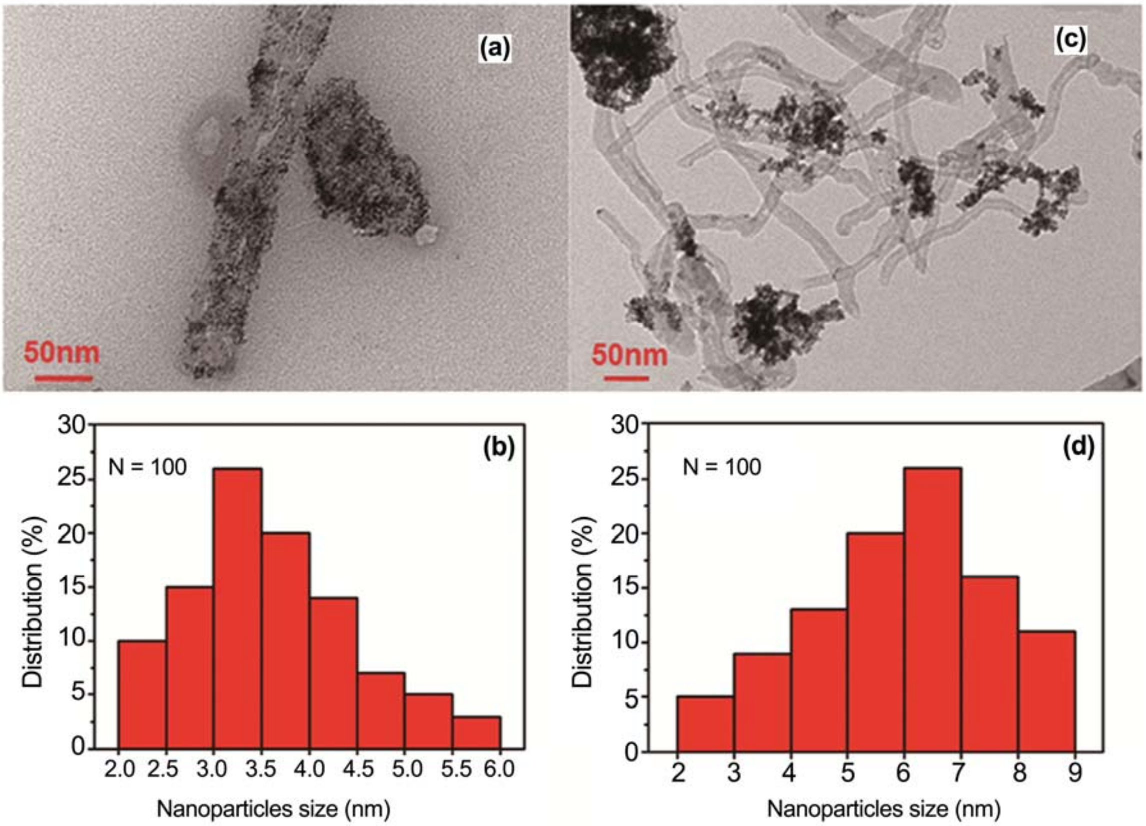


Fig. 3 — TEM images and size distributions of PtRu/CMS-CNTs (a, b) and PtRu/CNTs (c, d).

monolayer of H adsorbed on Pt surface[17]. The ESAs are 61.7 m^2 g^{-1} for PtRu /CMS-CNTs electrocatalysts and 40.9 m^2 g^{-1} for the PtRu/CNTs electrocatalysts. The former catalyst exhibits a relatively larger Pt surface area because the PtRu NPs dispersed on its surface have smaller average particle size (Fig. 3). The CV curves for PtRu/CMS-CNTs and PtRu/CNTs electrocatalysts in 0.5 M H_2SO_4 + 1.0 M CH_3OH solution are shown in Fig. 5. The forward peak current on the PtRu/CMS-CNTs electrocatalyst is 416.0 mA mg^{-1}, much higher than that 234.0 mA mg^{-1} on the PtRu/CNTs catalyst. On the other hand, the forward peak on set potential negatively shifts more than 250 mV relative to that of PtRu/CNTs electrocatalyst (140 mV). It is also noted that the forward peak potential of methanol oxidation on the PtRu/CMS-CNTs electrocatalyst (0.88 V vs. RHE) is more negative than that on other PtRu NPs supported on CNTs[18]. Also, the peak current of PtRu/CMS-CNTs is also higher than that of carbon black and the functionalized CNTs loading PtRu NPs recently reported as show in Table 2. Clearly, PtRu/CMS-CNTs electrocatalysts exhibit much improved electrocatalytic activities than that of the PtRu/CNTs electrocatalysts, which are apparently attributed to the smaller sizes, better dispersion, and higher ESA areas of the PtRu NPs.

Table 1 — The amounts of metal loading in PtRu/CMS-CNTs and PtRu/CNTs electrocatalysts measured by ICP-AES

Catalysts	Pt (wt.%)	Ru (wt.%)	Total (wt.%)
PtRu/CMS-CNTs	12.25	4.94	17.19
PtRu/CNTs	11.19	4.48	15.67

Table 2 — Comparison of the methanol oxidation activity for carbon nanotube supported catalyst active electrodes reported in literature

Electrocatalysts	Activity	Ref.
PtRu/1-AP-MWCNTs	295.0 $mA.mg^{-1}$ at 0.65 V vs. Ag/AgCl	[19]
Pt-PANI/MWNTs	19.55 $mA.cm^{-2}$ at 0.80 V vs. SCE	[20]
PtRu/PPA-CNTs	372.9 $mA.mg^{-1}$ at 0.64 V vs. SCE	[21]
PtRu/CNTs-PTCA	334.2 $mA.mg^{-1}$ at 0.64 V vs. SCE	[22]
PtRu /CNTs-DA	317.4 $mA.mg^{-1}$ at 0.65 V vs. SCE	[17]
PtRu/CMS-CNTs	416.0 $mA.mg^{-1}$ at 0.64 V vs. SCE	This work

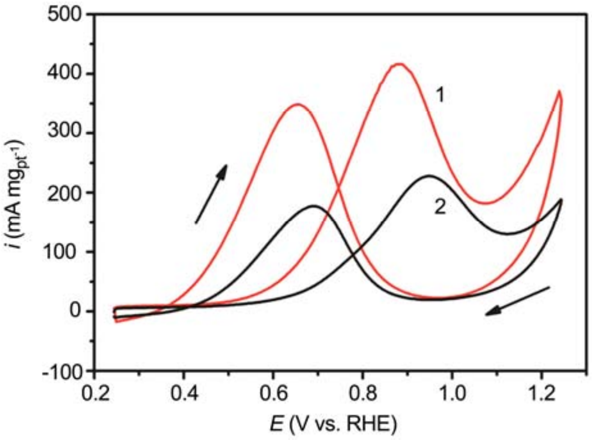


Fig. 5 — CV curves of PtRu/CMS-CNTs (1) and PtRu/CNTs (2) electrocatalysts in N_2- saturated solution of 0.5 M H_2SO_4 and 1.0 M CH_3OH at a scan rate of 50 mVs^{-1}.

We have further investigated the cycle stability of the electrocatalysts using CV technique. The plots of relative current density versus potential cycles for PtRu/CMS-CNTs and PtRu/CNTs electrocatalysts are shown in Fig. 6. For both electrocatalysts, their relative current density J/J_0 gradually decreases with increasing potential cycle. Upon 600 potential cycles, the PtRu/CMS-CNTs electrocatalyst retains about 87% of its intitial current density, while PtRu/CNTs can just retain 72%. To prove the reliability of this statement, our electrocatalysts on electrode surface for metals after 600 potential cycles was operated by using ICPES (Inductive Coupled Plasma Emission Spectrometer) and the results are summarized in Table 3. These results clearly indicate that the cycle stability of the PtRu/CMS-CNTs electrocatalyst is largely improved

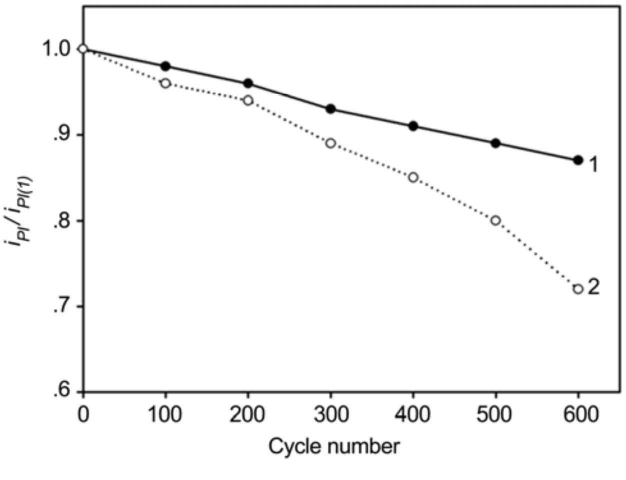


Fig. 6 — Plots of relative current density (J/J_0) versus potential cycles over a range of 0.64–0.70 V for PtRu/CMS-CNTs (1) and PtRu/CNTs (2) electrocatalysts in N_2-saturated solution of 0.5 M H_2SO_4 and 1.0 M CH_3OH.

Table 3 — The amounts of metal loading in PtRu/CMS-CNTs and PtRu/CNTs electrocatalysts on GC electrode upon 600 potential cycles measured by ICP-AES

Catalysts	Pt (wt.%)	Ru (wt.%)	Total (wt.%)
PtRu/CMS-CNTs	8.57	3.58	17.19
PtRu/CNTs	10.63	4.43	15.06

because the CNTs wrapped with CMS greatly prevent the PtRu NPs from detaching from the CNTs.

Conclusions

In summary, we have successfully prepared highly dispersed, small PtRu NPs on CNTs using conductive polymer CMS as surface linker. Owing to the highly dense and uniformly distributed terminal anchoring groups imparted by CMS, highly dispersed PtRu NPs with approximately diameter of 3 nm can be deposited on the CNTs. With synergistic effect from highly catalytic surface and ideal conductive triple-phase boundary among PtRu NPs, CMS, and CNTs, PtRu/CMS-CNTs electrocatalysts exhibit significantly enhanced catalysts and excellent long-term cycle stability toward MOR, showing great potential for practical application.

References

1 Basri S, Kamarudin S K, Daud W R & Yaakub Z, *Int J Hydr Ener*, 35 (2010) 7957.
2 Guo J W, Zhao T S, Prabhuram J, Chen R & Wong C W, *Electr Acta*, 51 (2005) 754.
3 Hsieh C T, Lin J Y & Yang S Y, *Phys E (Amsterdam Neth)*, 41 (2009) 373.
4 Li Z Z, Cui X L, Zhang X S, Wang Q F, Shao Y Y & Lin Y H, *Am J Nanosci Nanotech*, 9 (2009) 2316.
5 Xiong S X, Shi Y J, Chu J, Gong M, Wu B H & Wang X Q, *Electr Acta*, 127 (2014) 139.
6 Yoo E, Okada T, Kizuka T & Nakamura J, *J Power Sources*, 180 (2008) 221.
7 Yuan J H, Wang Z J, Zhang Y J, Shen Y F, Han D X, Zhang Q, Xu X Y & Niu L, *Thin Solid Films*, 516 (2008) 6531.
8 Zhang S, Shao Y Y, Yin G P & Lin Y H, *J Mater Chem*, 20 (2010) 2826.
9 Periasamy A P, Wu W P, Lin G L, Shih Z Y, Yang Z S & Chang H T, *J Mater Chem A*, 2 (2014) 11899.
10 Cheng Y, Xu C W, Shen P K & Jiang S P, *Appl Catal B*, 158 (2014) 140.
11 Yang D Q, Hennequin B & Sacher E, *Chem Mater*, 18 (2006) 5033.
12 Li C, Lee E K, Kim Y T & Lee D, *Int J Hydrog Ener*, 39 (2014) 17314.
13 Periasamy A P, Wu W P, Lin G L, Shih Z Y, Yang Z S & Chang H T, *J Mater Chem A*, 2 (2014) 11899.
14 Wang S, Jiang S P, White T, Guo J & Wang X, *J Phys Chem C*, 113 (2009) 18935.
15 Wu B H, Kuang Y J, Zhang X H & Chen J H, *Nano Today*, 6 (2011) 75.
16 Pozio A, De Francesco M, Cemmi A, Cardellini F & Giorgi L, *J Power Sources*, 105 (2002) 13.
17 Cui Y, Wu B H, MaoL Q & Yin D L, *Phys Stat Solid*, 209 (2012) 2532.
18 Palmer D, Levina M, Nokhodchi A, Douroumis D, Farrell T & Rajabi-Siahboomi A, *AAPS PharmSciTech*, 12 (2011) 862.
19 Wang S , Wang X & Jiang S P, *Langmuir*, 24 (2008) 10505.
20 Xu Y T, Lin S J, Peng X L, Luo W A, Gal J Y & Dai L Z, *Sci China: Chem*, 53 (2010) 2006.
21 Wu B H, Hu D, Kuang Y J, Yu Y, Zhang X & Chen J, *Chem Comm*, 18 (2011) 5253.
22 Meng L, Cao D, Liu W, Zhang Y & Zhao M, *Ionics*, 20 (2014) 1127.