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Rapid synthesis of water-soluble carbon nanotubes-supported PtRu nanoparticles for methanol electrooxidation

Bohua Wu [a,b,*], Chao Wang [a], Dong Xue [a], Jianliang Xiao [a,c]

[a] Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education and College of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, China
[b] College of Chemistry and Chemical Engineering, Xi'an University of Science & Technology, Xi'an, 710054, P.R. China
[c] Department of Chemistry, Liverpool Centre for Materials and Catalysis, University of Liverpool, Liverpool, UK

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ABSTRACT

A one-pot, rapid microwave-assisted method is proposed to directly synthesize water-soluble surface-aminated carbon nanotubes (CNTs-NH_2) from pristine CNTs by covalently grafting ethylenediamine onto the surface of CNTs, requiring no cumbersome chemical oxidation of CNTs. The excellent water-solubility and abundant surface functional groups of the CNTs-NH_2 lead to the production of uniformly dispersed PtRu nanoparticles (NPs) with diameter ranging from 1.5 to 4.5 nm. Cyclic voltammetry and amperometric studies indicate that the resulting PtRu NPs/CNTs-NH_2 nanohybrids have higher electrochemical surface area, better electrocatalytic performance and higher stability towards methanol oxidation compared to PtRu NPs supported on the pristine CNTs. The high electrocatalytic performance is mainly contributed to the small particle size and high dispersion of PtRu NPs and good proton conductivity of CNTs-NH_2. This work may demonstrate a universal approach to fabricate superior metal nanocrystalline on CNTs for broad applications in energy systems and sensing devices.

1. Introduction

Since they were reported by Iijima in 1991 [1], carbon nanotubes (CNTs) have aroused great interest owing to their unique mechanical, electronic, and optical properties as well as their potential applications for advanced materials and nanoscale devices [2–6]. Especially, hybrid materials based on the coupling of CNTs with noble metal nanoparticles (NPs) represent an emerging class of nanomaterials for multifunctional systems, since they possess the properties of the individual components with synergistic effects [6]. The resultant noble metal NPs/CNTs nanohybrids have been shown to exhibit interesting properties for promising applications in catalysis [7,8], electroanalysis [9,10], fuel cells [11–13], chem/biosensors [14,15], and surface-enhanced raman scattering [16]. For instance, Pt NPs/CNTs nanohybrids have been widely used as novel electrode materials in direct methanol fuel cells (DMFCs), showing higher catalytic activity and electrochemical stability as compared to the commercialized carbon black supported Pt catalyst (Pt/C) [11,17].

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 high specific surface area and are able to uniformly anchor and grow the metal NPs [18]. However, the technological development of noble metal NPs/CNTs nanohybrids have been hampered by the poor solubility of pristine CNTs in solvents, which originates from the strong van der Waals attraction among CNTs [2,3,6]. In addition, pristine CNTs do not have enough binding sites for anchoring noble metal precursors and growing noble metal NPs [19,20]. Consequently, noble metal NPs on the pristine CNTs generally have large particle size and poor dispersion, which is unfavourable for improving the overall catalytic activity of the noble metal NPs/CNTs nanohybrids. Furthermore, the poor interaction between the noble metal NPs and pristine CNTs cannot effectively prevent the noble metal NPs from Oswald ripening/aggregation during fuel cells operation, which results in poor durability of the noble metal NPs/CNTs catalysts and hence significant loss of the electrochemically active surface area (ESA) over time [21,22].

In order to solve the above issues, modulating surface properties of CNTs by covalent or noncovalent functionalization have been developed recently, resulting in CNT exfoliation and solubility in aqueous solution for further assembly of noble metal NPs. These strategies include chemical oxidation at defect sites of CNTs [23,24], wrapping of CNTs with polymers [19,25,26], grafting of ionic liquid [27] and modification of CNTs with 1-aminopyrene by π-stacking [20], and so on. Among these strategies, chemical oxidation is a simple and low-cost method which allows introduction of carboxyl groups to the CNT surface through an aggressive oxidation treatment with HNO_3 or a HNO_3/H_2SO_4 mixture. These carboxyl groups not only improve the hydrophilicity of CNTs but also effectively prompt the dispersion of the noble metal NPs on the CNT surface. However, this approach is often considered inferior due to a lack of good control of particle size and distribution of metal NPs as well as damage to the CNT structures.

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* Corresponding author. Tel./fax: +86 29 85310825.
E-mail addresses: wubohua2005@126.com (B. Wu), J.Xiao@liverpool.ac.uk (J. Xiao).

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On the other hand, chemical oxidation of CNTs is often used to graft amine-terminated functional molecules via amide bonds for achieving surface-aminated CNTs, e.g. CNTs-CONH-$(CH_2)_2$-NH_2 [28], CNTs-CONH-IL [27], and CNTs/DEN [29], which can anchor noble metal NPs on CNTs with some degree of control of particle size and size distribution. However, these previous methods for synthesis of surface-aminated CNTs are tedious and usually need multi-step procedures including carboxylation, chlorination/bromination and amination, etc [27–29]. The rigorous conditions and poor repeatability seriously limit their practical applications. Moreover, the amide bonds in the amino-functionalized CNTs are unstable under the common operation conditions of fuel cells, whose decomposition leads to noble metal NPs becoming easily dislodged from CNT surface and thus losing the durability of catalysts. So far, the direct synthesis of surface-aminated CNTs from pristine CNTs by a facile one-pot method for controllable assembly of noble metal NPs has seldom been reported and still remained a great challenge.

Herein, we report an alternative strategy to prepare surface-aminated CNTs (CNTs-NH_2) for deposition of small PtRu NPs on CNTs with uniform distribution. Different from the methods reported previously, our strategy is to directly functionalize pristine CNTs with ethylenediamine by a facile one-pot procedure (Scheme 1). In our system, ethylenediamine molecules are grafted on CNT surface by forming a semi-stable diazonium ion which then results in a radical reaction with CNTs under microwave radiation [30]. The introduction of high density and uniformly distributed -NH_2 groups not only improves solubility of pristine CNTs in water but also can effectively anchor and grow noble metal NPs via electrostatic and coordination of $PtCl_6^{2-}$ and Ru^{3+} with the $-NH_2$ group on CNTs. Usually, mixed proton-electron conducting materials should be ideal catalyst supports for DMFCs since they allow for low ohmic resistance in both the proton and electron conduction at the same time [25,31]. Due to the fact that $-NH_2$ group on CNTs can effectively transport protons, the surface-aminated CNTs facilitate proton conduction in an electron-conducting matrix, and it appears to be a promising material for construction of noble metal NPs/carbon nanotube nanohybrids. It is expected that PtRu NPs will be dispersed uniformly on the CNTs-NH_2 with small particle size and narrow size distribution, and the resultant catalysts (PtRu NPs/CNTs-NH_2) will show superb performance for the direct electro-oxidation of methanol. For comparison, PtRu NPs were supported on the pristine CNTs and the electrocatalytic properties of the PtRu NPs/CNTs catalysts for methanol oxidation were also investigated.

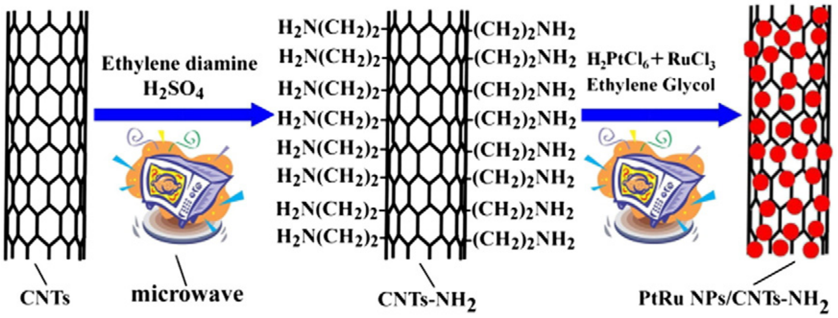
2. Experimental

Pristine multi-walled carbon nanotubes (CNTs) (length 5–15 μm, diameter 20–60 nm) were purchased from Shenzhen Nanotech Port Co. Ltd., China. $NaNO_2$ and ethylenediamine were purchased from Sinopharm chemical reagent Beijing Co. Ltd., China. Other chemicals were of analytical grade and used as received.

The procedure for preparing the surface-aminated CNTs (CNTs-NH_2) was as follows: the pristine CNTs (140 mg), ethylenediamine (5 mL), and $NaNO_2$ (188 mg) were ultrasonicated in 50 mL dimethylacetamide for 30 min, until a homogeneous suspension was obtained. After that, concentrated H_2SO_4 (0.5 mL) was added and the mixture was placed under microwave reaction. The abovementioned CNT suspension was heated in microwave up to 120 °C with output power of 800 W for 15 min. The resulting mixture was filtered through a nylon 66 membrane, and washed three times with distilled water. The final product, denoted as CNTs-NH_2, was then dried in a vacuum oven at 60 °C for 12 h.

Deposition of PtRu NPs on the CNTs-NH_2 was carried out via a microwave-assisted reduction process in ethylene glycol [26]. The details were as follows: 20 mg of CNTs-NH_2 was mixed with 438 μL aqueous solution of H_2PtCl_6 (38.6 mM) in ethylene glycol solution. After ultrasonication for 15 min, 350 μL aqueous solution of $RuCl_3$ (48.2 mM) was added into the mixture and ultrasonically 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 5 min at 140 °C. The product was centrifuged and washed three times with distilled water. The obtained PtRu electrocatalyst supported on the CNTs-NH_2, and denoted as PtRu NPs/CNTs-NH_2, was dried in vacuum oven at 60 °C for 12 h. For comparison, PtRu NPs supported on the pristine CNTs, labelled as PtRu NPs/CNTs, were prepared under the same procedure as described above.

The Pt and Ru loading of the PtRu NPs/CNTs-NH_2 (or PtRu NPs/CNTs) catalyst was determined by Inductively Coupled Plasma-Atom Emission Spectroscopy (ICP-AES, Spectro Ciros). Fourier transform infrared spectrometry (FTIR) (Nicolet, 6700) was employed to analyze the surface chemical compositions of the CNTs-NH_2. Raman spectrum (in Via, Renishaw, England) was also used to study the integrity and electronic structure of the samples. 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 ultrasonication. When a dark homogeneous dispersion was formed, a definite volume of the ink was dropped onto the GC electrode using micro-syringe. After drying 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.



Scheme 1. Schematic diagram of the surface-aminated CNTs and preparation of PtRu NPs/CNTs-NH_2 nanohybrids.

3. Results and discussion

Surface-functionalization of CNTs with ethylenediamine was characterized by FTIR. The FTIR spectra of ethylenediamine, pristine CNTs and CNTs-NH_2 are shown in Fig. 1. In the FTIR spectrum of ethylenediamine (curve 1 in Fig. 1), the peaks at 1628 cm^{-1} and 3480 cm^{-1} are consistent with ν(N–H) bending and stretching vibration of $-NH_2$ group, respectively. 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 peaks at 1576 cm^{-1} in the FTIR of CNTs-NH_2 (curve 3 in Fig. 1) is assigned to the ν(N–H) bending vibration of $-NH_2$ group, which indicates the successful functionalization of CNTs by ethylenediamine. Moreover, a very broad ν(O–H) bands stretching appeared in the range of 2000–3600 cm^{-1}, indicating that CNTs-NH_2 surface were also grafted with various $-OH$ groups, which may result from some defect sites of CNTs being oxidized by H_2SO_4 during the functionalization process.

The Raman spectroscopy was used to study the structure damage of the CNTs-NH_2. The corresponding results are shown in Fig. 2. It is noted that the peak at 1320 cm^{-1} is assigned to the A_{1g} breathing mode of disorder graphite structure (i.e., the D band), and the peak at ~1564 cm^{-1} assigned to the E_{2g} structure mode of graphite (i.e., the G band) [19]. The G band reflects the structure of the sp^2 hybridized carbon atoms. An additional side band at ~1600 cm^{-1} was also observed, which is assigned as the D′ band. 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) [19,20,26]. It is noted from Fig. 2 that the I_D/I_G ratio of CNTs-NH_2 is 1.79, which is much higher than that of the pristine CNTs (1.34). As reported previously [20], the value of I_D/I_G ratio of CNTs-AO (1.77) is slightly smaller than that of CNTs-NH_2. The higher I_D/I_G means the higher extent of covalent functionalization, the results from Fig. 2 imply that the functional groups on CNTs-NH_2 are more than those of pristine CNTs and CNTs-AO, and CNTs-NH_2 should be a promising support material for metal NPs in fuel cells.

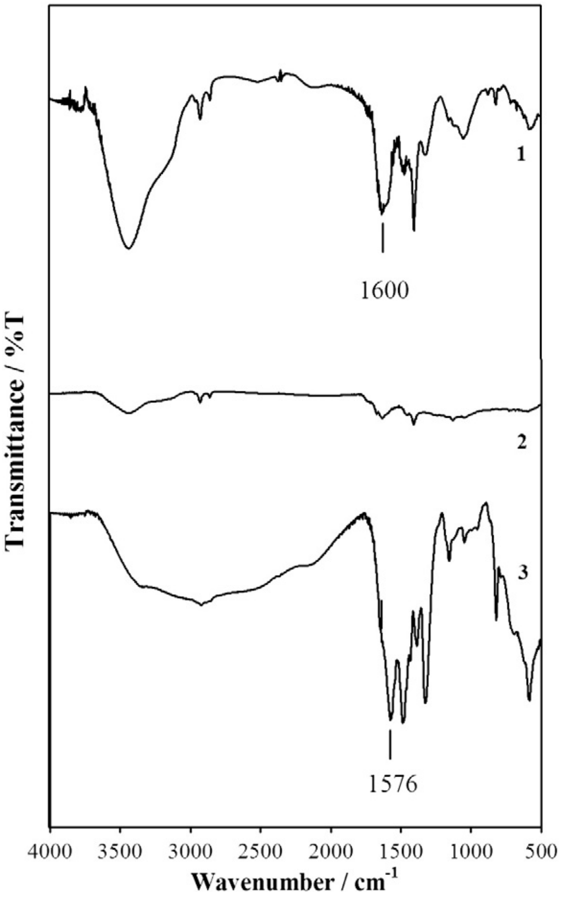


Fig. 1. FTIR spectra of ethylenediamine (1), pristine CNTs (2), and CNTs-NH_2 (3).

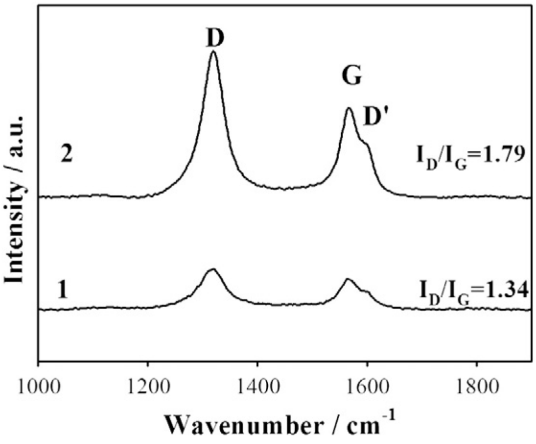


Fig. 2. Raman spectrum of pristine CNTs (1) and CNTs-NH_2 (2).

As mentioned above, the dispersibility of CNTs in solvents is one of the key issues for the deposition of metal NPs on CNTs [18]. Hence, a comparison of the dispersibility of CNTs-NH_2 and pristine CNTs in water was carried out and the corresponding results are shown in Fig. 3. As shown in Fig. 3, when 10 wt.% pristine CNTs in water were ultrasonicated for 30 min followed by sitting undisturbed for 24 h, aggregation and precipitation of nanotubes were observed at the bottom of the vial (Fig. 3, a1). In contrast, CNTs-NH_2 can easily and uniformly disperse in water and the well-dispersed CNT water solution showed no signs of phase separation after sitting undisturbed one month (Fig. 3, a2). This implies that the dispersibility of CNTs in water is greatly improved by the surface functionalization with ethylenediamine. Transmission electron microscopy (TEM) was used to further investigate the states of the dispersed CNTs, as shown in Fig. 3 b–c. In the 10 wt.% pristine CNT water solution, pristine CNTs exist mainly in the form of entangled bundles (Fig. 3b). However, when CNTs were functionalized with ethylenediamine, the CNT bundles were remarkably separated into individual nanotubes with a diameter of 20–60 nm (Fig. 3c). It is clear that ethylenediamine acts as a very efficient dispersing agent to debundle CNTs in water solution. This is most likely due to the hydrophilic surface $-NH_2$ groups interacting with water and so preventing aggregation of CNTs. The higher dispersion in water means a higher available specific surface area, and thus the $-NH_2$ group on CNTs-NH_2 is able to anchor and grow more metal NPs. It was expected that PtRu NPs will be dispersed uniformly on the CNTs-NH_2 with small particle size and narrow size distribution.

Fig. 4 shows the TEM images of the PtRu NPs/CNTs-NH_2 and PtRu NPs/CNTs nanohybrids. As can be seen, the PtRu NPs were all uniformly distributed on CNTs-NH_2 surface and did not aggregate with each other to form large clusters. 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 1.5 nm and 4.5 nm (with an average diameter of ca. 2.8 ± 0.5 nm). However, for the pristine CNTs, PtRu NPs do not disperse uniformly on the CNT surface and have a broad distribution (2.0–9.0 nm) with an average diameter of ca. 5.5 ± 1.0 nm. The reasons for this finding should be as follows. For the CNTs without surface modification, the defect sites generated during the growth and post-synthesis treatment of CNTs are usually not uniform. Furthermore, the poor dispersibility in solvents and the bundles states of pristine CNTs lead to insufficient available specific surface area for anchoring Pt and Ru precursors. When PtRu NPs are deposited on the pristine CNTs, PtRu NPs tend to deposit on these localized defect sites, thus leading

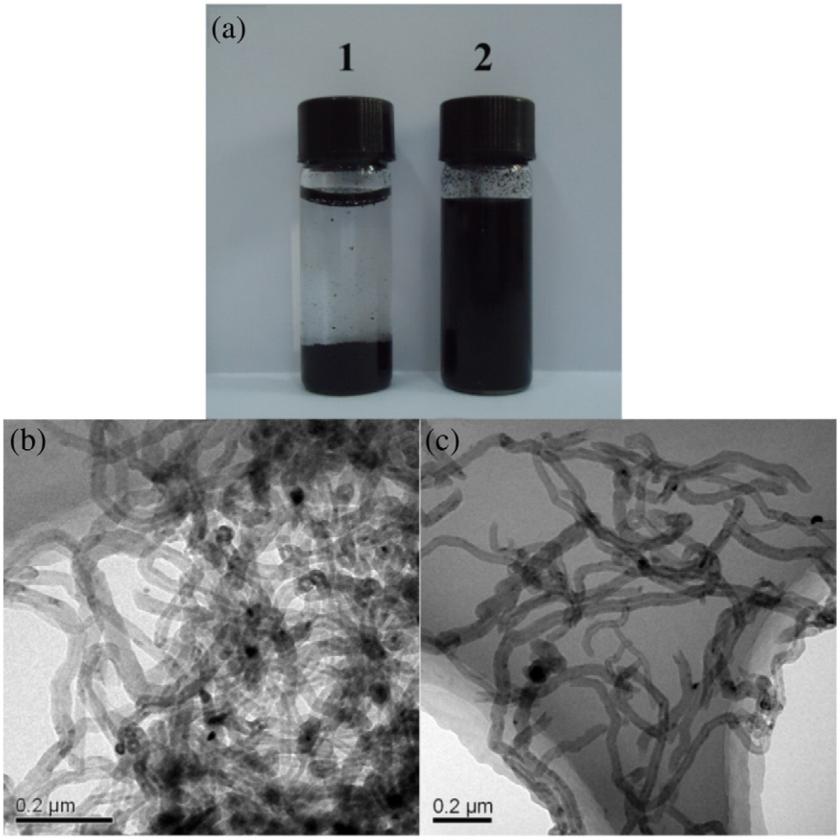


Fig. 3. Digital photographs of 10 wt.% pristine CNTs (a1) and CNTs-NH_2 (a2) dispersed in water for 24 h or one month, TEM images of 10 wt.% pristine CNTs (b) and CNTs-NH_2 (c) in water.

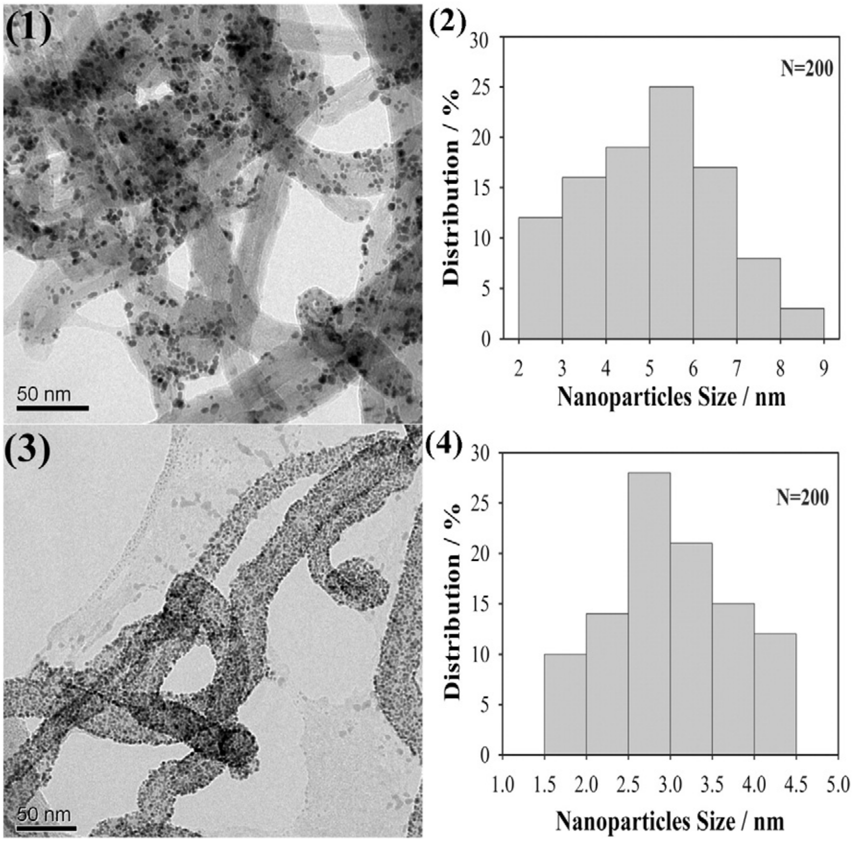


Fig. 4. TEM images and size distribution of PtRu NPs of PtRu NPs/CNTs (1, 2) and PtRu NPs/CNTs-NH_2 (3, 4) nanohybrids.

to poor dispersion and aggregation. However, for the CNTs with ethylenediamine modification, the ethylenediamine molecules on the surface of CNTs produce a large number of positively charged functional groups ($-NH_3^+$) with high density and uniform distribution that serve as the functional groups for the immobilization of Pt and Ru precursors on the CNT surface through electrostatic interactions. Therefore, a much more uniform distribution of PtRu NPs is observed on the surface of the CNTs-NH_2. The results of TEM indicate that high dispersion in water of CNTs-NH_2 and abundant surface functionalization groups play key roles in obtaining PtRu NPs with high dispersion and small particle size on the CNT surface.

The electrocatalytic performance of the PtRu NPs/CNTs-NH_2 nanohybrids as potential electrocatalysts for methanol electrooxidation was examined. Based on the ICP-AES results (Table 1), the total loading mass of Pt on glassy carbon electrode was adjusted to 23.70 $\mu g \cdot cm^{-2}$. Fig. 5 shows the cyclic voltammograms (CVs) of PtRu NPs/CNTs-NH_2 and PtRu NPs/CNTs nanohybrids measured in a nitrogen-saturated 0.5 M H_2SO_4 solution. Based on the hydrogen adsorption-desorption charges, the electrochemically active surface area (ESA) value of PtRu NPs supported on the CNTs-NH_2 or pristine CNTs can be calculated using the following equation [32]:

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

Where Q_H ($mC \cdot cm^{-2}$) represents the mean value between the amounts of charge exchanged during the electro-adsorption and desorption of H_2 on Pt sites, [Pt] is the Pt loading ($mg \cdot cm^{-2}$) on the electrode and 0.21 ($mC \cdot cm^{-2}$) represents the charge required to oxidize a monolayer of H_2 on bright Pt. The results show that the ESA value of the PtRu NPs/CNTs-NH_2 catalyst (95.8 $m^2 \cdot g^{-1}$ Pt) is 32.3% larger than that of PtRu NPs/CNTs catalyst (72.4 $m^2 \cdot g^{-1}$ Pt), which is attributed to the smaller particle size and much better dispersion of PtRu NPs on the CNTs-NH_2. This also demonstrates that the PtRu NPs deposited on the CNTs-NH_2 are electrochemically more accessible, which is very important for electrochemical oxidation reactions.

The electrochemical performance of the PtRu NPs/CNTs-NH_2 and PtRu NPs/CNTs catalysts in methanol electro-oxidation was investigated by cyclic voltammetry in nitrogen-saturated 0.5 M H_2SO_4 + 1.0 M CH_3OH aqueous solution and the results are shown in Fig. 6. Compared with PtRu NPs/CNTs catalyst, a significant enhancement of the peak current of methanol oxidation is observed on PtRu NPs/CNTs-NH_2 catalyst. The forward peak current of methanol oxidation on the PtRu NPs/CNTs-NH_2 catalyst is 572.1 $mA \cdot mg^{-1}$, being 1.4 times higher than that on the PtRu NPs/CNTs catalyst (397.6 $mA \cdot mg^{-1}$). On the other hand, the onset potential of methanol oxidation shifts more than 110 mV in negative direction when the catalyst support is changed from the pristine CNTs to CNTs-NH_2. These results show a noticeable feature that PtRu NPs/CNTs-NH_2 catalyst exhibits better electrocatalytic performance than PtRu NPs/CNTs catalyst. The reasons are as follows: (1) PtRu NPs/CNTs-NH_2 nanohybrids have the following superior features over the PtRu NPs/CNTs sample: smaller sizes, better dispersion and higher electrochemical surface area. (2) surface-aminated CNTs facilitate proton conduction in an electron-conducting matrix as the $-NH_2$ group on CNTs can effectively transport proton by forming $-NH_3^+$ in acid electrolyte [33], which is beneficial to form the "ideal" triple-phase boundary (TPBs) structure at the interface between PtRu NPs, $-NH_3^+$ group and CNTs to improve Pt utilization.

Table 1
The amounts of metal loading in PtRu NPs/CNTs-NH_2 and PtRu NPs/CNTs nanohybrids measured by ICP-AES.

Catalysts	Pt (wt.%)	Ru (wt.%)	Total (wt.%)
PtRu NPs/CNTs-NH_2	11.63	4.55	16.18
PtRu NPs/CNTs	9.87	4.35	14.37

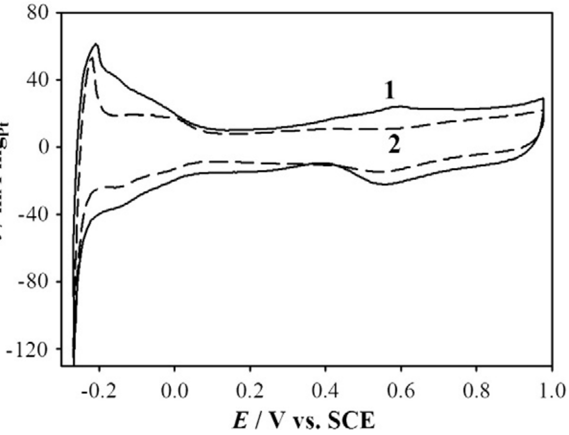


Fig. 5. Cyclic voltammograms of PtRu NPs/CNTs-NH_2 (1) and PtRu NPs/CNTs (2) nanohybrids in nitrogen-saturated 0.5 M H_2SO_4 aqueous solution at a scan rate of 50 mVs^{-1}.

The stability of the PtRu NPs/CNTs-NH_2 and PtRu NPs/CNTs catalysts towards methanol electro-oxidation was investigated by amperometric *i-t* test at a fixed potential of 0.5 V for 3600 s in nitrogen-saturated 0.5 M H_2SO_4 + 1.0 M CH_3OH aqueous solution and the results are shown in Fig. 7. The PtRu NPs/CNTs-NH_2 catalysts retain a current density of 61.3 $mA \cdot mg^{-1}$ at 3600 s, which is much higher than that of PtRu NPs/CNTs catalyst (15.0 $mA \cdot mg^{-1}$), indicating that PtRu NPs/CNTs-NH_2 catalyst is more suitable for long-term operation. Five repetitive measurements on PtRu NPs/CNTs-NH_2 catalyst gave a standard deviation of 8.2%, showing good reproducibility of the catalyst.

In practical applications, the long-term cycle stability of the catalysts is of great importance [34,35]. In this work, the long-term cycle stabilities of PtRu NPs/CNTs-NH_2 and PtRu NPs/CNTs catalysts have also been investigated in 0.5 M H_2SO_4 + 1.0 M CH_3OH aqueous solution by cyclic voltammetry and the corresponding results are shown in Fig. 8. It can be observed that the value of i/i_0 decreases gradually with the successive scans. In the case of PtRu NPs/CNTs-NH_2 nanohybrids, the peak current at 500th cycle is about 89% of that measured at the first cycle. The decrease of i/i_0 on PtRu NPs/CNTs-NH_2 is only 16% for 500 cycles. However, for the PtRu NPs/CNTs catalyst, a large decrease (32%) is found. This implies that the long-term stability of PtRu NPs/CNTs-NH_2 catalyst is higher than that of the PtRu NPs/CNTs catalyst, which agrees with the results of amperometric *i-t* test. The excellent stability of PtRu NPs/CNTs-NH_2 catalyst may result from that ethylenediamine

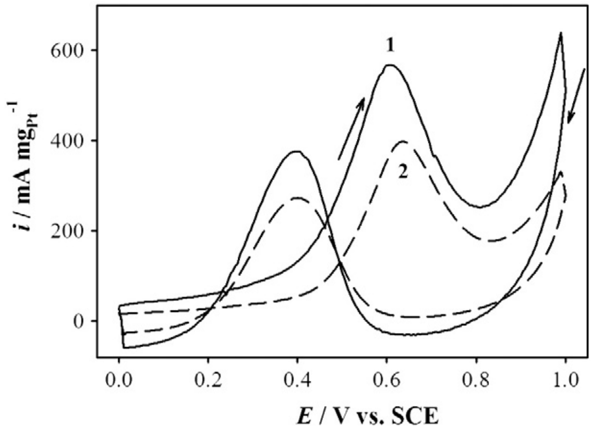


Fig. 6. Cyclic voltammograms of PtRu NPs/CNTs-NH_2 (1) and PtRu NPs/CNTs (2) nanohybrids in nitrogen-saturated 0.5 M H_2SO_4 + 1.0 M CH_3OH aqueous solution at a scan rate of 50 mVs^{-1}.

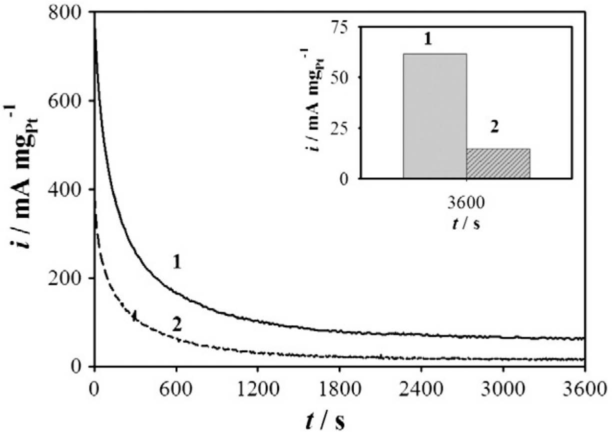


Fig. 7. Amperometric i-t test of PtRu NPs/CNTs-NH_2 (1) and PtRu NPs/CNTs (2) nanohybrids in nitrogen-saturated 0.5 M H_2SO_4 + 1.0 M CH_3OH aqueous solution at 0.5 V.

molecules can effectively stabilize and anchor PtRu NPs on the surface of CNTs via the electrostatic and coordinative actions between PtRu NPs and positively charged functional groups ($-NH_3^+$) on the CNT surface.

4. Conclusions

In summary, we have successfully developed a facile one-pot method for direct synthesis of surface-aminated CNTs from pristine CNTs and the functionalized CNTs can be used as support for noble metal NPs. Thanks to the excellent dispersion of CNTs-NH_2 in water and its abundant surface functionalization groups, small PtRu NPs with an average diameter of ca. 2.8 ± 0.5 nm were uniform deposited on CNTs surface. Compared to PtRu NPs/CNTs nanohybrids, PtRu NPs/CNTs-NH_2 nanohybrids toward methanol electrooxidation exhibit significantly enhanced catalytic current density, lower oxidation peak potential, and longer-term operation stability, due to the small particle size and high dispersion of PtRu NPs on CNTs-NH_2, and good proton conductivity of CNTs-NH_2. The CNTs-NH_2 should be promising catalyst supports for noble metal NPs in fuel cells.

Prime novelty statement

Based on a one-pot, rapid microwave-assisted method, water-soluble surface-aminated carbon nanotubes (CNTs-NH_2) were directly synthesized from pristine CNTs by covalently grafting ethylenediamine onto the surface of CNTs, requiring no cumbersome chemical oxidation of CNTs. Due to their excellent water-solubility, abundant surface functional groups and the excellent proton conductivity, the platinum-ruthenium nanoparticles (PtRu NPs) were highly dispersed on the CNTs and the obtained PtRu NPs/CNTs-NH_2 nanohybrids show superb performance for methanol electrooxidation.

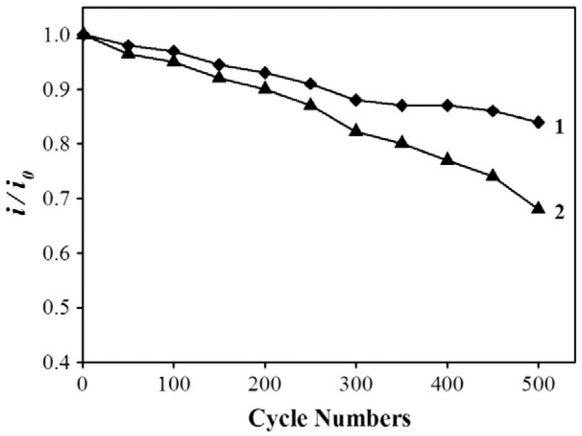


Fig. 8. Long-term cycle stabilities of PtRu NPs/CNTs-NH_2 (1) and PtRu NPs/CNTs (2) nanohybrids in nitrogen-saturated 0.5 M H_2SO_4 + 1.0 M CH_3OH. i/i_0, measured as the ratio of forward peak current at the nth cycle and the forward peak current at the first cycle.

Acknowledgments

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