Pt–Ni bimetallic composite nanocatalysts prepared by using multi-walled carbon nanotubes as reductants for ethanol oxidation reaction

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A B S T R A C T
The multi-walled carbon nanotubes (MWNTs) are introduced as reductants to prepare bimetallic PtNi x composite nanocatalysts via a hydrothermal reaction for the investigation of ethanol oxidation reaction (EOR). The crystal structure and elemental analysis of PtNi x/MWNTs nanocatalysts are characterized by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS), respectively. The morphologies of these nanocatalysts are observed by transmission electron microscopy (TEM) and scanning electron microscope (SEM). The results reveal that the PtNi x nanocatalysts with a nanoparticle size ranging from 6 to 13 nm are immobilized on the surface of MWNTs. The electrocatalytic activities of the PtNi x/MWNTs nanocatalysts for EOR in alkaline media are examined using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA). The onset potential of EOR in the nanocatalyst of PtNi 3/MWNTs is negatively shifted for about 190 mV as compared to that in the nanocatalyst of Pt/MWNTs. The current for the forward anodic peak of EOR in the PtNi 3/MWNTs nanocatalyst is about 2.5 times higher than that of pure Pt/MWNTs.

Introduction
Recently, the low-temperature fuel cells such as direct alcohol fuel cells (DAFCs) are attracting considerable attention. They serve as eco-friendly techniques to produce electricity by direct electrochemical conversion of the organic molecules and oxygen into water and carbon dioxide. Among various kinds of fuel cells, direct ethanol fuel cell (DEFC) is considered as a promising power source not only for portable electronics devices but also for electric vehicles due to its high energy density (8.0 kWh kg⁻¹), green emission and ambient operation conditions [1]. Ethanol is easier to transport than hydrogen and less toxic than other alcohols such as methanol. Also, ethanol can be produced in large quantities from agricultural products such as sugar cane, wheat and corn [2]. Therefore,
developing novel catalysts towards ethanol oxidation reaction (EOR) has turned into a hot topic in the research field of electrochemistry. Although platinum (Pt) has been recognized as the best catalyst for EOR at low temperature, it can be easily poisoned by reaction intermediates due to a strong interaction between CO and the Pt surface [3]. Therefore, a number of Pt-based binary or ternary catalysts, such as Pt–Sn [4], Pt–Ru [5], Pt–Pd [6], Pt–Sn–Mo [7], Pt–Pb–Bi [8], are generated towards EOR with the low cost while maintaining the high electrocatalytic activity toward EOR compared to the Pt catalyst alone. However, except the work done by Ko et al. [9], there are few papers regarding the electrocatalytic activity of Pt–Ni bimetallic catalyst toward the EOR in alkaline media. Only some related works have been reported on the Pt–Ni bimetallic catalysts for methanol oxidation reaction (MOR), oxygen reduction reaction (ORR) and formic acid oxidation reaction (FAOR) [10–18].

Up to now, two typical methods for generating Pt–Ni nanoparticles have been developed. One is the chemical reduction reaction. For example, Wu et al. [12] reported the preparation of graphene-supported hollow Pt–Ni nanocatalysts, in which K2PtCl6 and NiCl2·6H2O were utilized as the precursors and NaBH4 a reducing reagent. In this work, the electrocatalysis of Pt–Ni toward methanol oxidation reaction (MOR) in a H2SO4 solution was investigated. Another one is the electrochemical reduction reaction [19]. Habibi et al. [20] synthesized Pt–Ni alloy nanoparticles at potential of −0.4 V vs. a saturated calomel electrode (SCE) from an 0.1 M Na2SO4 aqueous solution containing H2PtCl6, 5H2O and NiCl2, and studied the electrooxidation of 2-propanol and 2-butanol on this alloy nanoparticles in an acidic media. However, the preparation of Pt–Ni nanoparticles by a facile process of hydrothermal reaction has not been reported so far.

Although Pt–Ni bimetallic or alloy nanoparticles have been widely applied for MOR, the reasons for the introduction of Ni to increase the currents and to reduce the onset potential for methanol oxidation on Pt–Ni electrodes are still unclear. For example, Mathiyarasu et al. [13] studied the MOR in a 0.5 M H2SO4 solution and proposed that the surface redox species Ni oxide, which were formed during the electro-oxidation process due to the oxygenation of COads, were contributed to the improvement of oxidation current of MOR. However, Abdel Rahim et al. [14] suggested that in the presence of Ni, the number of active sites of Pt was increased through an electron donation process from Ni to Pt and this led to a lower density of states at the Fermi level. This may promote the electrocatalytic performance of Pt [21]. Although many works concerning Pt–Ni materials have been published recently [22–26], the exact catalytic mechanism of Pt–Ni catalyst towards the oxidation of small organic molecules is still unknown.

As a typical catalyst support for fuel cells, carbon nanotubes (CNTs) attract a great deal of attention due to its unique properties, such as high specific surface area, electrical conductivity, and good thermal and chemical stability [27] compared to other carbon materials, such as graphene and carbon nanofiber [28,29]. Anchoring metal nanoparticles on CNTs has turned into an interesting research topic because of the key roles of CNTs and metal nanoparticles in the field of electrocatalysis, biosensors [30]. To the best of our knowledge, the immobilization of Pt–Ni composite nanoparticles onto CNTs by a hydrothermal reaction method without adding any other reductants has not been published yet, though we have successfully immobilized Pt nanoparticles on the surface of multi-walled carbon nanotubes (MWCNTs) [31].

In this work, five kinds of PtNi/MWCNTs nanocatalysts with different molar ratios of Pt to Ni have been prepared by a hydrothermal reaction without introducing any other reductants. The PtNi/MWCNTs nanocatalysts have been characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscopy (TEM). The electrocatalytic activities of the nanoparticles for EOR are investigated through cyclic voltammetry (CV) and chronoamperometric curves. The mechanism for the electrocatalytic performance enhancement of PtNi/MWCNTs catalyst towards EOR in alkaline solution was discussed in details.

**Experiment**

**Materials**

Deionized water was used to prepare the aqueous solutions. MWCNTs (purity >95%) with diameter of 10–20 nm diameter were purchased from Shenzhen nanotech port Co., Ltd. (China). All electrodes were obtained from Tianjin Aida Co., Ltd (China). All other chemicals were analytical grade and used without further purification.

**Preparation of PtNi nanoparticles onto MWCNTs**

3 mL 5 × 10−3 M H2PtCl6·6H2O and an appropriate amount of Ni(CH3COO)2·4H2O were dissolved in deionized water with a molar ratio of Pt to Ni of 1:1, 1:2, 1:3 and 1:4, respectively. Then 10 mg MWCNTs were added into the above solution and ultrasonicated for 30 min. The resultant suspension solution was placed in a well-sealed autoclave at room temperature and transferred to a box-type furnace. The temperature of the furnace was increased to 200 °C within 30 min and kept for 2 h to accomplish the hydrothermal reaction process. The hydrothermal reaction process was implemented in a SRJX-8-13 box-type furnace equipped with a KSY 12-16 furnace temperature controller. After cooling down to room temperature, the filtered samples were thoroughly washed with deionized
water and dried in ambient conditions to generate the PtNi/MWNTs nanocatalysts. The Pt/MWNTs and Ni/MWNTs catalysts were also prepared by the same procedure in the absence of Ni(CH₃COO)₂·4H₂O or H₂PtCl₆·6H₂O.

**Fabrication of PtNi/MWNTs modified electrode**

The working electrodes were prepared by coating catalyst ink onto a glassy carbon (GC) electrode. GC electrode (geometric area is 0.07 cm²) was polished with 0.05 μm alumina suspensions before each experiment and served as a substrate for the working electrode. The catalysts ink was prepared by dispersing 1 mg catalyst in 1 mL of 0.1 wt% Nafion ethanol solution. After ultrasonication for 10 min, about 15 μL catalyst ink was added on the surface of the GC electrode and slowly dried in air to produce a PtNi/MWNTs-coated GC electrode.

**Characterization**

The morphology of the as-prepared PtNi/MWNTs nanocatalysts was observed by scanning electron microscope (Hitachi, SEM S-570) and transmission electron microscopy (Hitachi, TEM H-7650). Energy Dispersive X-Ray Spectroscopy (EDS) spectrum analysis was carried out on a X-ray energy instrument (EDAX, PV-9900, USA). XRD analysis of the nanocatalysts was performed on a Bruker D8 ADVANCE X-ray diffractometer equipped with a Cu Kα source (λ = 0.154 nm) at 40 kV and 30 mA. The 2θ angular region between 10 and 90° was explored at a scan rate of 1°/step.

All the electrochemical measurements were performed on a CHI 660B electrochemical workstation (Shanghai Chenhua Apparatus, China) connected to a personal computer. Electrochemical impedance spectroscopy (EIS) was performed in a 1 M ethanol in 1 M KOH solution. After ultrasonication for 10 min, about 15 μL catalyst ink was added on the surface of the GC electrode and slowly dried in air to produce a PtNi/MWNTs-coated GC electrode.

**Results and discussion**

**XRD and EDS analyze**

XRD measurements were employed to characterize the crystalline structures of the Pt–Ni nanocatalysts. The results are presented in Fig. 1. The diffraction peaks located at 24.8° in the XRD patterns are assigned to the (002) face of MWNTs [31]. In the XRD pattern of the Pt/MWNTs nanocatalyst, four peaks at 2θ values of about 39.9, 47, 68 and 82° correspond to the planes of (111), (200), (220) and (311), respectively. These four peaks, characterized by the face-centered-cubic (fcc) crystalline Pt (JCPDS, No.01-087-0646 Card), are consistent with the previous report [31,32] very well. This indicates that Pt⁴⁺ ions could be reduced by this hydrothermal reaction process in the presence of MWNTs without other reductants. For the Ni/MWNTs catalyst, no characteristic peaks of Ni or its oxides/hydroxides are detected, indicating that the amount of Ni nanoparticles or its oxides/hydroxides is too less or exists in amorphous phases [33]. Interestingly, in the XRD patterns of PtNi/MWNTs, PtNi₂/MWNTs, PtNi₃/MWNTs and PtNi₄/MWNTs, only the characteristic diffraction peaks of the fcc Pt are exhibited. This suggests that the addition of Ni has no obvious effect on the crystal structure of Pt. It is evident that the diffraction peak intensities of the Pt are sharply decreased with increasing the molar ratio of Ni in the PtNi nanocatalysts. For example, the PtNi₄/MWNTs nanocatalyst shows the weakest diffraction peak among the obtained PtNi/MWNTs nanocatalysts. Meanwhile, there is no obvious peak shift observed in the XRD patterns for all the prepared nanocatalysts, indicating that Ni is hard to alloy with Pt using the hydrothermal reaction method [21]. This means that the as-prepared PtNiₓ/MWNTs nanocatalysts were composite rather than alloy nanoparticles.

The average crystallite size of these nanocatalysts are calculated based on the X-ray line widths of Pt (111) reflection using Scherrer equation as shown in Equation (1) [34]:

\[
L = \frac{k\lambda}{\beta \cos \theta}
\]

where k is a shape factor (0.9), λ is the wavelength of X-ray (1.54056 Å), β is the width of the half maximum full-width and θ is the Bragg angle at position of maximum peak. The calculated crystallite sizes of the nanoparticles based on the plane of (111) for PtNi/MWNTs, PtNi₂/MWNTsand PtNi₃/MWNTs are 53.9, 53.8 and 46.1 nm, respectively. The crystallite sizes calculated based on Equation (1) are much larger than those estimated from TEM images, Fig. 3B. This is because that XRD can only reflect crystalline nanoparticles rather than the actual morphology of catalysts, and large nanoparticles are selected in XRD patterns, while most of the small nanoparticles are counted in TEM images [35].
EDS analysis is performed to explore the chemical composition of the as-prepared samples. The typical EDS spectrum of PtNi/MWNTs is illustrated in Fig. 2. In Fig. 2, the peaks corresponding to C, O, Pt and Ni elements are clearly displayed and no other elements are detected. The atomic contents of Pt and Ni are 0.47 and 0.77%, respectively. Thus, the obtained molar ratio is smaller than that of the starting materials used in the experiments. The metallic Ni is hard to form since in the stable suspension and solid state, the nickel nanoparticles are very sensitive to air [36], the element Ni would exist in the form of Ni oxides or hydroxides.

**Morphology observation**

The obtained SEM and TEM images of the pure MWNTs and PtNi/MWNTs nanocatalysts are presented in Fig. 3A and B. Compared to the pure MWNTs, Fig. 3A-(a), some dots are observed to be anchored on the surface of MWNTs for all the PtNi/MWNTs nanocatalysts after the hydrothermal reaction process, Fig. 3A-(b–f). This result strongly demonstrates that the hydrothermal reaction method is feasible to produce metal particles-coated MWNTs. This method may be employed to synthesize metal-particles/MWNTs hybrid systems in a large scale. As shown by the red-circled part in all the images, much smaller nanoparticles are fabricated on the surface of MWNTs in the PtNi/MWNTs nanocatalyst (Fig. 3A-(e)) compared to other samples (Fig. 3A-(b–d and f)).

As illustrated in Fig. 3B, the detailed morphologies of five nanocatalysts are characterized by TEM. Compared to pure MWNTs, Fig. 3B-(a), some nanoparticles are decorated on the surface of MWNTs for all the nanocatalysts. Based on the TEM images shown in Fig. 3B, the nanoparticle sizes for the catalysts of Pt, PtNi, PtNi2, PtNi3 and PtNi4 are around 12.5, 11.5, 10.0, 6.0 and 13.0 nm, respectively. Evidently, the nanoparticle size on the nanocatalyst of PtNi3/MWNTs is the smallest among all the catalysts, which may provide a larger surface area when the loadings of added nanoparticles is exhibited in the catalyst of PtNi3/MWNTs. This result proves that the molar ratio of Pt to Ni in the nanocatalysts played a key role in determining the morphologies of the as-prepared nanocatalysts.

**Electrochemical behavior**

The cyclic voltammograms (CVs) of nanocatalyst PtNi/MWNTs in 1 M KOH containing 1 M ethanol are shown in Fig. 4A. No evident oxidation peaks of EOR are found on the MWNTs and Ni/MWNTs, implying that MWNTs and Ni have no electrocatalytic ability towards EOR. However, EOR proceeded obviously on the catalysts of Pt/MWNTs and PtNi/MWNTs. There are two oxidation peaks in the CVs of the Pt/MWNTs catalyst. One is located at around −0.26 V on the anodic scan (peak f) and another one is positioned at about −0.41 V on the cathodic scan (peak b). These results are consistent with the prior report [38]. Interestingly, for the sample of PtNi/MWNTs, the oxidation peaks currents of EOR are significantly improved in comparison with Pt/MWNTs. The oxidation peak current of EOR on the anodic scan in the catalyst of PtNi/MWNTs is about 2.5 times larger than that obtained in the nanocatalyst of Pt/MWNTs. In addition, the onset potential for peak f towards EOR is negatively shifted for about 190 mV in the nanocatalyst of PtNi/MWNTs compared to that of Pt/MWNTs nanocatalyst. Close inspection indicates that compared to the Pt/MWNTs nanocatalyst, the oxidation peak potentials of EOR for peak f and peak b in the PtNi/MWNTs nanocatalyst are negatively shifted about 40 and 45 mV, respectively.

The CV curves of EOR in various kinds of PtNi/MWNTs nanocatalysts are displayed in Fig. 4B to evaluate the effect of Ni content on the electrocatalytic activity of PtNi/MWNTs. Despite the catalyst of PtNi/MWNTs, all the Ni-doped catalysts showed improved electrocatalytic activities towards EOR as compared to that of the Pt/MWNTs based on the peak currents of EOR. Generally, the anodic peak current in the forward scan indicates the oxidation current of freshly chemisorbed species and the current arising from the reverse scan stands for the oxidation of the carbonaceous species [39]. Thus, the ratio of the forward anodic peak current (peak f) to the reverse anodic peak current (peak b), f/b, can be used to evaluate the poisoning tolerance of a catalyst [39]. A larger f/b ratio indicates a better ethanol oxidation ability during the anodic scan and less accumulation of carbonaceous residues on electrode surface. The value of f/b ratio for Pt/MWNTs, PtNi/MWNTs, PtNi2/MWNTs, PtNi3/MWNTs and PtNi4/MWNTs is estimated to be 4.51, 2.45, 2.40, 1.12 and 4.20, respectively. This result illustrates that more carbonaceous residues are accumulated on the nanocatalyst of PtNi/MWNTs. However, the largest peak currents of EOR are obtained in the nanocatalyst of PtNi3/MWNTs, Fig. 4B. Meanwhile, the results acquired from chronoamperometric curves in Fig. 4C substantially verify that the nanocatalyst of PtNi3 possesses the highest electrocatalytic activity among all the nanocatalysts. This result is contrary to the previous assumption. The similar results have also been addressed in many published papers. For example Wang’s group [40] found that the catalytic activity of the Pt–Ni/C catalyst was higher for...
methanol electro-oxidation than that of the Pt–Ru/C catalyst, however, in the CVs of MOR, the ratio of peak f to peak b for the Pt–Ru–Ni/C catalyst was smaller than that of the Pt–Ru/C catalyst. Zhao and his workers [41] reported that the addition of Ir could significantly improve the ethanol oxidation kinetics on Pd in alkaline media. The Pd7Ir/C catalyst exhibited the higher activity and stability than the other samples whereas the peak current ratio of \( I_f/I_b \) was not increased too much for the Pd7Ir/C catalyst compared with that of the pure Pd/C catalyst.

In this work, two novel parameters are proposed tentatively to evaluate the electrocatalytic ability of a catalyst. One is defined as electrocatalytic intensity (EI). The electrocatalytic intensity of a catalyst towards EOR can be represented by a total current of peak f and peak b at a potential scanning rate, \( E_I = I_f + I_b \). This parameter may reflect the whole reaction rate of EOR on a catalyst. The values of \( E_I \) for Pt/MWNTs, PtNi/MWNTs, PtNi2/MWNTs, PtNi3/MWNTs and PtNi4/MWNTs are calculated to be 147.7, 178.9, 260.1, 579.1 and 92.9 \( \mu A \), respectively. Evidently, the catalyst of PtNi3/MWNTs displays the highest reaction rate in all the resultant catalysts, Fig. 4B. Although peak f and peak b in EOR correspond to different oxidation mechanisms, it has been widely accepted that both peak f and peak b are all resulted from the oxidation of ethanol or the intermediates produced in the process of EOR. Therefore, another parameter of electrocatalytic quantity, \( E_Q \), is proposed, and defined as the area sum of peak f and peak b at a potential scan rate in CV test. In other words, the area sum of the forward and backward peak in CV of EOR should correspond to the total amount of electrooxidized substances. The values of \( E_Q \) for Pt/MWNTs, PtNi/MWNTs, PtNi2/MWNTs, PtNi3/MWNTs and PtNi4/MWNTs are estimated to be 0.23, 0.49, 0.71, 1.56, and 0.23 mC, respectively. It is evident that the order of \( E_Q \) for the as-prepared samples is consistent with the electrocatalytic activities exhibited by the prepared nanocatalysts very well. That means that the nanocatalyst of PtNi3/MWNTs has the best electrocatalytic activity among all the samples.

Generally, the forward peak current and onset potential are two parameters that can reflect the electrocatalytic activity of a catalyst toward EOR [42]. The forward peak current and onset potential for Pt/MWNTs, PtNi/MWNTs, PtNi2/MWNTs, PtNi3/MWNTs, PtNi4/MWNTs and PtNi5/MWNTs are approximately 123 \( \mu A \) and \(-0.42 \) V, 127 \( \mu A \) and \(-0.65 \) V, 184 \( \mu A \) and \(-0.66 \) V, 305 \( \mu A \) and \(-0.67 \) V, 75 \( \mu A \) and \(-0.47 \) V, respectively. These results show that the nanocatalyst of PtNi3/MWNTs has the largest forward peak current and the most negative onset potential of EOR.
Based on the above analysis, at least three conclusions can be achieved: (1) a proper amount of Ni doped Pt can significantly enhance the electrocatalytic ability of Pt towards EOR; (2) the doped Ni element may effectively influence the onset potential of EOR, which indicates that the process of EOR on the PtNi_x nanocatalysts is much different from that on the pure Pt catalyst; (3) the molar ratio of Pt to Ni was a key factor that substantially affects the electrocatalytic activity of the resultant PtNi_x nanocatalysts towards EOR.

The long-term stabilities of the prepared catalysts with various Pt/Ni molar ratios are valued by using chronoamperometric measurement [43]. Fig. 4C presents the current—time plots of all the catalyst electrodes in 1 M KOH containing 1 M ethanol at a potential of —0.28 V. It is observed that all the current—time curves are consisted of two stages. In the first stage of 50 s, the currents drop quickly mainly due to the accumulation of CO-like intermediates on the surface of the nanocatalyst. In this stage, these adsorbed species may occupy many free Pt active sites and prevent ethanol molecules from further adsorption and oxidation. After this stage, the currents drop slowly and the electrode reactions reach a steady state because of the fact that the adsorption of oxygenated and poisonous species as well as their redox reactions has attained a relative balance [44]. The largest value of steady current is observed in the PtNi_3/MWNTs nanocatalyst within the whole testing period, which implies that the catalyst of PtNi_3/MWNTs has the best electrocatalytic ability and catalytic durability among all the prepared catalysts. This result may be attributed to the smaller nanoparticle size and uniform dispersion of PtNi_3 on the surface of MWNTs, Fig. 3B.

In the electrochemical impedance spectroscopy (EIS) measurement, Nyquist plot can be used to evaluate the electrochemical performance of a working electrode [45] directly. Fig. 5A illustrates the Nyquist plots of all the nanocatalysts in the solution of 1 M KOH containing 1 M ethanol at the open circuit potential (OCP). Generally, the semicircle displayed in the high frequency region corresponds to a circuit having a resistance element parallel to a capacitance element [46]. The straight line in the low frequency region is attributed to the Warburg impedance. In Fig. 5A, instead, a half semicircle is observed in the high frequency region which is very similar to the previous report [47]. This is probably due to the lower value of the upper limiting frequency used. Usually, the semicircle diameter equals the charge transfer resistance \( R_{ct} \). A bigger semicircle corresponds to a larger value of \( R_{ct} \), and the lower the value of \( R_{ct} \), the faster the charge transfer reaction rate will be. The values of the semicircle diameter for PtNi_x/MWNTs, PtNi_2/MWNTs, PtNi_3/MWNTs and PtNi_4/MWNTs estimated from Fig. 5A are approximately 6.1, 4.2, 3.4, and 6.9 \( \Omega \), respectively. The lowest value of \( R_{ct} \) in the PtNi_3/MWNTs electrode suggests that the charge transfer process of EOR occurring on the catalyst of PtNi_3/MWNTs is faster than those on other nanocatalysts.

Bode plots for all the samples are also illustrated in Fig. 5B aiming to attain more useful information on the electrochemical properties of the as-prepared catalysts. Evidently, only the PtNi_3/MWNTs coated GC electrode at a scan rate of 100 mV \( s^{-1} \) in 1 M KOH containing 1 M C_2H_5OH solution showed two symmetric peaks within the applied frequency region. Normally, the symmetric peak in Bode plot may correspond to a relaxation process of the electrode/solution interface [48]. Therefore, there are two relaxation processes of the electrode/solution interfaces in the PtNi_3/MWNTs due to the existence of two phases in the PtNi_3. One phase is the Pt phase and...
another phase is Ni oxides or hydroxides. Consequently, the properties of Pt and Ni oxides or hydroxides are both displayed. This can be employed to interpret the strange behavior of PtNi₃/MWNTs observed in the CP test (Fig. 6). In addition, the Bode plots for all other nanocatalysts are observed different from each other. This indicates that the structure of PtNiₓ/MWNTs-coated GC electrode is strongly affected by the molar ratio of Pt to Ni. The lower phase angle of the PtNi₃/MWNTs coated GC electrode (20.8°/C₁₄ at 0.1 Hz) is obtained compared to other samples (66.8, 57.0, 51.0, 55.0°/C₁₄ at 0.1 Hz for Pt, PtNi, PtNi₂ and PdNi₄/MWNTs, respectively). This may be interpreted that the PtNi₃/MWNTs nanocatalyst exhibits less capacitive behavior than other samples since ideal capacitive systems should give phase angles of 90° [49,50].

To study the electrocatalytic activity and stability of the as-prepared nanocatalysts for the EOR in alkaline media, chronopotentiometry (CP) tests are performed and the results are given in Fig. 6. In the CP tests, a constant current density of 0.3 mA cm⁻² is applied for 1800 s. Theoretically, the electrode potential will increase after applying a positive current. The polarization potential is observed to increase within the testing period for all the PtNiₓ/MWNTs-coated GC electrodes, Fig. 6, whereas the shapes of CP curves are different from each other. Interestingly, Pt/MWNTs and PtNi/MWNTs have the analogous shapes of CP curves due to the close components presented in these two samples. However, for the PtNiₓ/MWNTs-coated GC electrode, the polarization potential is increased sharply from −2.0 V to 2.2 V within 130 s. Then the potential is decreased gradually to a constant value of 2.0 V at 450 s. For the PtNiₓ/MWNTs-coated GC electrode, no evident potential peak is observed within the whole period. This result strongly indicates that the above two electrodes proceed in a much different way when a positive current was applied. Surprisingly, a different shape of CP curve is shown in the catalyst of PtNi₃/MWNTs. At the initial stage, the polarization potential of electrode is slowly increased from 2.0 V at 0 s to 0.3 V at 1290 s. Then the potential is increased sharply to a constant value of 2.19 V at the time of 1610 s. Lastly, the value of electrode potential is fixed at 2.20 V. Thus, the stability of PtNi₃/MWNTs is the best one among all the samples. Meanwhile, the slope of CP curve of PtNi₃/MWNTs demonstrates that the PtNi₃/MWNTs nanocatalyst electrode is not an ideal polarizable electrode compared to other used electrodes. This means that some electrochemical reactions have happened on the PtNiₓ/MWNTs nanocatalyst electrode when being charged by a positive current [51]. On the other hand, due to the lower standard electrode potential of Ni²⁺/Ni (0.257 V vs. NHE) [52], Ni is easy to lose electrons and form Ni²⁺. This means that due to the electrochemical reaction between the Ni and the hydroxyl ion, Ni + 2OH⁻ → Ni(OH)₂ + 2e⁻, Ni(OH)₂ can be formed on the electrode [53]. When the applied voltage is increased further, Ni peroxide is formed immediately following the formula, Ni(OH)₂ → NiOOH + H⁺ + e⁻ [47]. The newly formed NiOOH may act as electron transfer mediator for the oxidation process, NiOOH + alcohol → Ni(OH)₂ + products [54]. This may be responsible for the excellent electrocatalytic ability of PtNiₓ/MWNTs nanocatalyst towards EOR compared to other nanocatalysts. In addition, in Fig. 6, the PtNiₓ/MWNTs nanocatalyst...
shows the lowest polarization potential among all the nano-catalysts within the whole measured period. Therefore, the addition of a proper amount of Ni to Pt can greatly facilitate the removal of the adsorbed ethoxi intermediates and make it more resistant to poisoning. To further clarify the electro-catalytic mechanism of the PtNi3/MWNTs catalysts towards EOR, more intensive studies are required to explain the contribution of Ni and its oxides to EOR.

Meanwhile, according to the electrochemical theory, a mini-cell may form in the as-prepared catalysts, in which Ni is used as the negative electrode and Pt as the positive electrode, respectively. The formed micro-battery can change the micro-environment of the interface between the PtNi3/MWNTs and electrolyte and generate a significant effect on the process of EOR. This concept may provide a possible interpretation for explaining the fact that many binary or ternary composite particles of catalysts have excellent electrocatalysis towards reactions in fuel cells [4–7].

In order to understand the mechanism of the catalyst formation, photos of the filtered solutions before and after the hydrothermal reaction are shown in Fig. 7A. A light brown solution containing PtCl$_6^{2−}$ ions before the hydrothermal reaction is clearly observed in Fig. 7A-a. Interestingly, after the hydrothermal reaction, the filtered solution turned to colorless, which indicates that all ions of Pt$^{4+}$ are reduced in the process of hydrothermal reaction. Meanwhile, in the solution having the ions of PtCl$_6^{2−}$ and Ni$^{2+}$, a colorless solution is observed after the hydrothermal reaction. This implies that all the ions in the solution have been reduced during the hydrothermal reaction. It is noticed that in the absence of MWNTs, no color changes in the solution after hydrothermal reaction are observed, which effectively proves that MWNTs are employed as the reductants in the process. Normally, the carbon surface is often decorated with oxygen containing functional groups due to the self-oxidation, which represents as compounds such as carboxylic acids, phenols, lactones, carboxylic anhydrates, ketones, ethers, quinones or pyrones [55]. In addition, in the presence of deionized water and MWNTs, a reductive environment can be produced by the some reactions between water and carbon such as C$+$H$_2$O$\rightarrow$CO$+$H$_2$ [56]. This means that the produced CO and H$_2$ are the reductants, which can reduce the formed metal oxides during the process of hydrothermal reaction. In other words, a reducing environment is created by the system containing MWNTs and water. Therefore, the reaction between the metal ions and MWNTs may proceed easily, though the exact reaction mechanism of this process cannot be only clarified by these photos.

Correspondingly, the ultraviolet–visible (UV–vis) absorption spectra of the solution before and after the hydrothermal reaction process are presented in Fig. 7B. For the aqueous solution having PtCl$_6^{2−}$ before the hydrothermal reaction process as shown in curve a, an absorption peak at around

![Fig. 7 - A Pictures of H$_2$PtCl$_6$ solution (a) before and (b) after the hydrothermal reaction process; pictures of H$_2$PtCl$_6$ and Ni(CH$_3$COO)$_2$ solution (c) before and (d) after the hydrothermal reaction process. B UV–vis spectra of H$_2$PtCl$_6$ solution (a) before and (b) after the hydrothermal reaction; H$_2$PtCl$_6$ and Ni(CH$_3$COO)$_2$ solution (c) before and (d) after the hydrothermal reaction process.](image)
260 nm is clearly observed, which is consistent with the previous report [57]. However, after the hydrothermal reaction, no obvious absorption peaks are observed within the whole measured wavelength range. It strongly indicates that all the PtCl$_6^{2-}$ ions have reacted with the introduced MWNTs, leading to the formation of Pt nanoparticles on the surface of MWNTs. For the solution containing PtCl$_6^{2-}$/C$_0$ and Ni$^{2+}$, except a maximum absorption peak appearing at 259 nm, a weak absorption peak at around 210 nm is seen. This peak may probably correspond to the $n$/$\pi^*$ (or $\pi$/$\pi^*$) transition of C=O bonds in the group of CH$_3$COO [57]. Unfortunately, the absorption peak located around 390 nm corresponding to the ions of Ni$^{2+}$ [57] is not displayed. This may be due to the fact that it is difficult to separate Ni$^{2+}$ from Ni(CH$_3$COO)$_2$ compared to NiCl$_2$ based on the ionization theory of acids and bases. Obviously, the intensities of all the absorption peaks significantly decreased after the hydrothermal reaction process. This suggests that the amount of ions is lowered due to the formation of PtNi$_x$ nanoparticles. These results demonstrate that the introduced ions of PtCl$_6^{2-}$/C$_0$ and Ni$^{2+}$ are reduced to generate metallic nanoparticles in the presence of MWNTs through the facile method of hydrothermal reaction. Why did the PtNi$_x$ catalysts containing different molar ratios of Pt to Ni present such different electrocatalytic activity towards EOR? In order to further explore the possible reasons for this question, CVs of five typical nanocatalysts including Pt, PtNi, PtNi$_2$, PtNi$_3$, and PtNi$_4$ in 1 M KOH are plotted in Fig. 8A. Generally, the electrochemically active surface area (EASA) of a catalyst is a key parameter to influence its activity towards EOR. It is well known that the method of integrating the CV curves in the H adsorption/desorption region of PtNi$_x$ catalysts can be employed to calculate the value of EASA approximately by the following equation (2) [58]:

$$\text{EASA} = \frac{(Q_H)}{(M_{Pt(PtNi_x)} / Q_{ref})}$$

(2)

where $Q_H$ is the amount of charges from the oxidation of the hydrogen atoms on the Pt or PtNi$_x$ surface, $M_{Pt}$ stands for the mass of Pt loading, and $Q_{ref}$ represents the hydrogen (H) adsorption charge on a smooth platinum electrode (0.21 mC cm$^{-2}$) [58]. However, the accurate value of $M_{Pt}$ cannot be obtained with our present techniques. Thus, the value of EASA can only be estimated approximately by assuming that the weights of various nanocatalysts are identical. As a result, the values of EASA show the following decreasing order: PtNi$_3$ > PtNi$_2$ > PtNi$_4$ > PtNi > Pt. This result indicates that the nanocatalyst of PtNi$_3$ has higher electrocatalytic activity than other Pt–Ni samples as well as pure Pt. Meanwhile, it is noted that for the nanocatalyst of Pt/MWNTs, according to the previous report, the reduction peak located at around $-0.41$ V could be assigned to the reduction of platinum oxides [59]. Evidently, the onset potentials of this peak are shifted positively for all the Ni-doped nanocatalysts relative to that of pure Pt catalyst. This suggests that platinum oxides formed on the PtNi$_3$ nanocatalysts can be reduced facilely compared to that on pure Pt. Obviously, among all the prepared nanocatalysts, the PtNi$_3$ shows the largest peak current and the most positive onset potential for the reduction peak of
platinum oxides. Therefore, when the polarization potential of the catalyst electrode is altered from −0.75 to 0.2 V vs. SCE, more active Pt sites can be released on the PtNi3 nanocatalyst in comparison with other samples. This may be partially responsible for the excellent electrocatalytic performance of PtNi3/MWNTs towards EOR.

As shown in Fig. 8A, the onset potential of hydrogen adsorption for PtNi3 nanocatalyst is the most positive among all the nanocatalysts. The potential window of CV test is changed from 0.2−1.0 to 0.2−1.2 V to further understand the hydrogen evolution behavior on various nanocatalysts. Surprisingly, as shown in Fig. 8B, a huge hydrogen evolution peak (green line) located at around −1.2 V is presented on the PtNi3 though the behavior of hydrogen evolution on the PtNi3 is also clearly observed. It has been proposed that Ni can activate water molecules and provide preferential sites for OH adsorption (H2O −→ OHads + H+ + e−) at lower potential than Pt, and the abundant -OHads species are good for completely oxidizing the CO product to CO2 (COads + OHads → CO2 + H+ + e−) to avoid the electrode poisoning [9]. However, in this case, a reduction process of water molecule, H2O + e− → OH− + H, is displayed on the catalyst of PtNi3. Probably, similar to the above assumption, a proper amount of Ni doped in Pt may activate water molecules to generate hydrogen atom or gas easily at more positive potential than Pt. Thus, more OH− groups are formed on the surface or in the vicinity of the PtNi3 nanocatalyst. This may lead to an accelerated process of CO2 formation due to the increased concentration of OH− groups.

To prove that a proper amount of the newly formed −OH groups is beneficial to the EOR, the electrode potential of PtNi3/MWNTs-coated GC electrode is kept at −0.75 V vs. SCE for a period and the electrode potential is scanned from −0.75 to 0.2 V by a linear sweep voltammetry (LSV) technique. All the results are illustrated in Fig. 8C. The peak current of the forward peak for EOR is greatly increased with increasing time. For instance, the peak current of EOR obtained at 20 s-period is around 1.4 times larger than that without potential (−0.75 V) treatment. Meanwhile, the onset potential of the peak for EOR is negatively shifted for the curve of 20 s compared to that of the curve of 0 s. However, when the potential treatment exceeds 30 s, the peak current of EOR was decreased quickly. According to the CV curves shown in Fig. 8A, it is confirmed that the hydrogen evolution has taken place as the electrode potential approached −0.75 V. As the potential treatment period is increased to 30 s, more hydrogen atoms or gases are produced on the surface of the nanocatalyst. The adsorption process of ethanol molecules on the nanocatalyst surface may be hindered, which leads to a lowered electro-oxidation process of ethanol.

Conclusion

In this work, PtNi3 nanoparticles have been prepared by a facile hydrothermal reaction method with MWNTs as reductants and the electrocatalytic behavior of these nanoparticles have been studied. XRD patterns testified the immobilization of PtNi3 nanoparticles with a face centered cubic (fcc) crystalline state on the surface of MWNTs and the PtNi3 nanocatalyst has the smallest particle size around ~6 nm among all the as-prepared samples. The electrocatalytic measurements revealed that the catalyst of PtNi3/MWNTs is a good material for ethanol oxidation in alkaline medium compared to other PtNi3 nanocatalysts. A decreased 190 mV for the onset potential and a 2.5 times enhancement for the peak current are observed in PtNi3/MWNTs compared to Pt/MWNTs. Among these prepared PtNi3 nanocatalysts, the smaller nanoparticle size and uniform dispersion are recognized as the main reasons for the improvements in electrocatalytic activity and stability of PtNi3 towards EOR. Meanwhile, two parameters including E1 and E2 are proposed for the first time to estimate the electrocatalytic ability of a catalyst towards EOR. In addition, it was found that the process of hydrogen evolution on the catalyst of PtNi3/MWNTs is much easier than other nanocatalysts. Most importantly, the PtNi3/MWNTs nanocatalyst shows the lowest value of polarization potential among all the prepared samples when being charged by a positive current in the CP tests. The facile hydrothermal reaction method is expected to be utilized as a technique for preparing Pt−Ni bimetallic nanoparticles in a large scale.

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