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Core/shell Ni@Pd nanoparticles supported on MWCNTs at improved electrocatalytic performance for alcohol oxidation in alkaline media

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ABSTRACT

Ni@Pd nanoparticles with core/shell structure uniformly dispersed on multi-walled carbon nanotubes (Ni@Pd/MWCNTs) is successfully prepared via a two-step strategy: impregnation-reduction method and replacement method. The Ni@Pd/MWCNTs composite was characterized by transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) analysis. It shows a uniform dispersion of Ni@Pd nanoparticles with core/shell structure on MWCNTs with the average particle size of 3.4 nm. The Ni@Pd/MWCNTs composite was used as electrocatalyst for alcohol oxidation in alkaline media for fuel cells. The electrocatalytic activity of ethanol oxidation on Ni@Pd/MWCNTs is 2.3 times higher than that of Pd/MWCNTs electrocatalyst at the same Pd loadings. The enhanced electrocatalytic properties could be attributed to not only the electric synergistic effect between Pd and Ni, but also the high use ratio of Pd for its shell structure.

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1. Introduction

Fuel cell technology has been considered as an effective way to solve the problem of the exhaustion trend for fossil fuel. However, the high cost has been remaining the choke point in the popular application of fuel cells, especially the high cost of the noble metal supported electrocatalyst, which is one of the most critical units in fuel cell systems [1]. To decrease the use level of noble metal at the condition of remaining or increasing the electrocatalytic activity is of great significance.

One solution is to disperse the noble metal nanoparticles with less size by using various supports which could greatly improve the use ratio of noble metal and electrocatalytic activity [2–6]. Carbon materials with various shapes and structures have been adopted as electrocatalst support due to its low weight, high specific surface area and chemical inertia. Yan et al. [7] synthesized three kinds of hollow carbon hemispheres, which showed highly improved dispersion, use ratio and mass transportation for Pd electrocatalyst. Owing to the better electrical conductivity and chemical stability, carbon nanotubes (CNTs) have attracted numerous studies in electrocatalyst support. Wang et al. [8] reported a facile room temperature wet chemical approach toward single-crystal platinum nanocubes/CNTs heterostructures with high dispersion and the assynthesized CNTs supported Pt electrocatalyst displayed excellent activity toward the oxygen reduction reaction. Another solution is to develop cheap catalyst promoter which could remarkably improve the overall catalytic activity through the way of synergistic effect between the promoter and noble metal [9–11]. The alloy that composed of noble metal and transition metal has been found higher electrocatalytic activity than simple noble metal electrocatalyst, which is explained as synergistic effect between the two metals [12–17]. Therein, the core/shell structure with noble metal as shell and base transition metal as core has more advantages. As catalytic reactions occur on the surface of the nanoparticles, a large fraction of metal in the core of the nanoparticle is wasted. Consequently, a noble metal at outer surface and base metal second atomic layer instead of noble metal as electrocatalyst are of great significance for the use level improvement of noble metal.

There have been lots of methods for preparing core/shell nanoparticles [18–22,14,23–35]. Wang et al. [16] synthesized PdCo@Pd/C nanoparticles with core/shell structure using H₂-induced surface segregation effect. They found that the PdCo@Pd/C electrocatalyst showed much higher methanol tolerances than Pt/C when being used in oxygen reduction reaction. Lu et al. [24] synthesized Au–Pd core/shell nanocrystals with tetrahexahedral structure by using Au nanocubes as structure-directing cores and found high electrocatalytic activity. Another well known method is the spontaneous galvanic replacement technique that was proposed by Adzic and Kokkinidis [25–35]. According to this method, core/shell bimetallic electrocatalysts with monolayer noble metal shell on noble metal or non-precious metal core can be prepared [36–38]. However, most of the synthesized noble metal based core/shell nanoparticles have thicker noble metal shell than that of the simple

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noble metal particles reported. Zhao et al. [15] have successfully synthesized Ni@Pd nanoparticles on multi-walled carbon nanotubes by one-step, but the Ni@Pd nanoparticles they synthesized show an uneven distribution on MWCNTs, which in fact could not increase the use ratio of noble metal.

Recently, Pd-based electrocatalysts have aroused much attention because they can be highly active for the alcohol oxidation in alkaline media where many non-noble metals are stable for electrochemical applications [39,40]. The mechanistic study on the electrooxidation of ethanol on Pd has also been reported based on an in situ FTIR spectroelectrochemical study [41].

Herein, Ni@Pd core/shell nanoparticles supported on MWCNTs (Ni@Pd/MWCNTs) and its electrocatalytic properties for alcohol oxidation were studied. The Ni@Pd/MWCNTs has uniform dispersion of Ni@Pd nanoparticles with the average particle size of 3.4 nm indicating less thickness of Pd shell. We applied the Ni@Pd/MWCNTs to catalyzing alcohol oxidation, where the possible origin of the high activity of Ni@Pd/MWCNTs was discussed.

2. Experimental details

2.1. Preparation of acid-functionalization of MWCNTs

MWCNTs used in this work were purchased from Shenzhen Nanotechnologies Port Co. Ltd. (Shenzhen, China) with the diameter of 20–40 nm, lengths of 6–15 mm, and purity of 98%. The MWCNTs were purified in nitric acid solution by the ultrasonic treatment for 30 min, refluxed with concentrated nitric acid at 100 °C for 12 h, then washed and filtered with deionized water [42,43]. In order to generate lots of functional groups on the surface of MWCNTs, the typical treatment was as follows [44,45]: H_2SO_4/HNO_3 (3:1) and MWCNTs were mixed with sonication for 10 min, then placed in an oil bath at 80 °C for 1 h. The resulting product was filtered and washed with deionized water for several times, and dried in a vacuum oven at 60 °C for 12 h.

2.2. Preparation of Ni/MWCNTs composite

Nickel nanocrystals deposited on MWCNTs were prepared by impregnation–reduction method using a vacuum quartz tube furnace (OTF-1200X system) at the temperature of 600 °C [46–48]. Briefly, MWCNTs were thoroughly dispersed into a saturated nickel nitrate aqueous solution and settled for two days at room temperature. Then the product was dried at 130 °C, and subsequently calcined at 600 °C for 30 min under nitrogen atmosphere, and finally the nickel impregnated MWCNTs (Ni/MWCNTs) were obtained. The Ni contents of were analyzed by inductively coupled plasma spectroscopy (ICP, Optima2000DV, USA) analysis, which showed 16.4 wt.% of Ni in Ni/MWCNTs compound.

2.3. Preparation of Ni@Pd/MWCNTs electrocatalyst

Ni@Pd/MWCNTs nanosized electrocatalysts were synthesized using replacement method. Typically, 10 mL of 0.186 mol/LH₂PdCl₄ and 2 g Ni/MWCNTs were dispersed in 50 mL distilled water in beaker. The resulting solution was uniformly dispersed by sonification for 10 min, and then vigorously stirred for 14 h at room temperature. The black solid was separated by sintered discs, washed with deioned water for several times, and finally dried in a vacuum oven at 60 °C. For comparison, Pd nanoparticles supported on MWCNTs (Pd/MWCNTs) as electrocatalyst was also obtained directly by reducing the H₂PdCl₄ in MWCNTs suspension using formic acid as reducing agent. The theoretical Pd contents in both Ni@Pd/MWCNTs and Pd/MWCNTs were targeted at 10 wt.%. The ICP



Fig. 1. Schematic diagram of the synthesis of Ni@Pd nanocatalysts on MWCNTs.

analysis gave the actual Pd contents as 9.7 wt.% for Ni@Pd/MWCNTs and 9.2 wt.% for Pd/MWCNTs, respectively.

2.4. Preparation of catalyst electrode

For electrode preparation, 20.6 mg Ni@Pd/MWCNTs or 21.7 mg Pd/MWCNTs were dispersed in 1 mL ethanol and 1 mL 0.5 wt.% Nafion suspension (DuPont, USA) under ultrasonic agitation to form the electrocatalyst ink. The electrocatalyst ink (40 μ L) was then deposited on the surface of the glassy carbon rod and dried at room temperature overnight. The total Pd loadings were controlled at 0.02 mg cm⁻². All chemicals were of analytical grade and used as received.

2.5. Characterization of the supports and the electrocatalysts

The morphology of the as-prepared samples were examined by a field emission scanning electron microscopy instrument (SEM, Hitachi S-4800 II, Japan) and transmission electron microscopy (TEM, JEOL-JEM-2010, Japan) operating at 120 kV. The structures of the obtained samples were examined by X-ray diffraction (XRD) using D8 Advance X-ray diffraction (Bruker axs company, Germany) equipped with Cu-KR radiation (λ) 1.5406 (Å), employing a scanning rate of 0.02° s⁻¹ in the 2 θ range from 10° to 80°.

All electrochemical measurements were performed in a threeelectrode cell on an IM6e potentiastat (Zahner-Electrik, Germany) at 30 °C controlled by a water-bath thermostat. A platinum foil (1.0 cm^2) and Hg/HgO $(1.0 \text{ mol } \text{dm}^{-3} \text{ KOH})$ were used as counter and reference electrodes, respectively.

3. Results and discussion

3.1. The formation mechanism of Ni@Pd/MWCNTs

The schematic illustration for the formation of Ni@Pd/MWCNTs nanocomposite is shown in Fig. 1. Once acid-MWCNTs were thoroughly dispersed into a saturated nickel nitrate aqueous solution and settled for two days at room temperature, the nickel-impregnated MWCNTs were formed. The calcination at 600 °C under nitrogen atmosphere could make Ni-impregnated MWCNTs transformed into monocrystalline nickel nanoparticles (Ni/MWCNTs). After the Ni/MWCNTs being added in H₂PdCl₄ solution and continuously stirred for 14 h, well dispersed Ni@Pd nanoparticles with core/shell structure on MWCNTs were obtained.

3.2. Morphology and element analysis

The morphology and element distribution of Ni@Pd nanoparticles were examined by TEM and EDS as shown in Fig. 2. A large number of extremely small nanoparticles dispersed homogeneously on the surface of the MWCNTs (Fig. 2B) comparing with the smooth surface of none supported MWCNTs (Fig. 2A). The Ni@Pd nanoparticles on the MWCNTs have a narrow diameter range from 2 to 5 nm. The HRTEM image describing the crystalline nature of Ni@Pd nanoparticles is shown in Fig. 2C. The single crystalline



Fig. 2. TEM images of acid-treated MWCNTs (A), Ni@Pd/MWCNTs (B), HRTEM images of Ni/MWCNTs (C), EDS spectrum of Ni@Pd/MWCNTs composites (D), TEM images of Pd/MWCNTs (E) and EDS spectrum of Pd/MWCNTs composites (F).

Ni@Pd particles are confirmed, the lattice planes with a interlayer distance of 0.203 nm in the core are indexed to Ni (111) crystal planes, the outer layer with the lattice space of 0.224 nm corresponds to Pd (1 1 1) crystal planes. Besides, Pd nanoparticles supported on MWCNTs with the diameter range of 3–4 nm could be observed from Fig. 2D. The elemental analysis by EDS proved that the Ni@Pd/MWCNTs is composed of C, Ni and Pd (Fig. 2E, the Cu signal comes from the sample holder, and the O signal comes from the oxidation of surfacial metal atom), however, the Pd/MWCNTs has no Ni signal (Fig. 2F).

3.3. XRD analysis

The crystal structure of MWCNTs, Ni/MWCNTs, Pd/MWCNTs and Ni@Pd/MWCNTs were determined by XRD as shown in Fig. 3A. The broad peaks at $2\theta = 26.1^{\circ}$ are associated with C (002) planes of

the graphite-like structure of the MWCNTs. The peaks at 2θ of 44.8°, 52.0° and 76.6° correspond to the Ni (1 1 1), (2 0 0) and (2 2 0) crystal planes, and the peaks at 2θ of 40.3, 46.8 and 68.3 correspond to Pd (1 1 1), (2 0 0) and (2 2 0) crystal planes, respectively. It is important that no diffraction peaks of their oxides were detectable and the high and sharp peaks indicted their well crystallinity. The Scherer's equation was used to calculate the crystal size of Pd:

$$D = \frac{RR}{B\cos\theta}$$

where *D* presents the average diameter in nm, *K* presents the Scherrer constant (0.89), λ presents the wavelength of X-ray ($\lambda = 0.154056$ nm), *B* presents the corresponding full width at half maximum (FWHM) of the (220) diffraction peak, and θ presents the Bragg's diffraction angle. The Pd particle size was calculated from all the Pd (111), (200) and (220) crystal plane parameters and averaged as 3.4 nm and 3.8 nm for Ni@Pd/MWCNTs and



Fig. 3. (A) The XRD patterns of CNTs, Ni/CNTs, Pd/CNTs and Ni@Pd/CNTs. (B)-(D) The enlarged XRD patterns of Pd/MWCNTs and Ni@Pd/MWCNTs at different diffraction angles.

Pd/MWCNTs respectively, which are very close to the TEM results.

Besides, as it is displayed in Fig. 3B–D, positive shift of the Pd peaks occurs obviously on the Ni@Pd/MWCNTs comparing with the Pd/MWCNTs, indicating the Ni atoms enter into the Pd crystals which caused the narrow transformation of the Pd crystal lattice distance. Kadirgan et al. [49] reported that the variation of crystal lattice parameters of noble metal could obviously improve its catalytic activities.

3.4. Ni@Pd/MWCNTs as electrocatalysts for alcohol oxidation

Fig. 4A shows the cyclic voltammograms of ethanol, methanol and isopropanol oxidation on Ni@Pd/MWCNTs electrodes. The Ni@Pd/MWCNTs electrocatalyst shows extremely high activity for the ethanol oxidation in terms of the onset potential and peak current density in comparison with methanol and isopropanol in alkaline solution. For ethanol oxidation, the Ni@Pd/MWCNTs shows 2.3 times peak current density as high as that on Pd/MWCNTs electrocatalyst at the same Pd loadings as shown in Fig. 4B. Fig. 4C indicated that the mass activity of the ethanol oxidation in 1 moldm⁻³ ethanol solution on Ni@Pd/MWCNTs was 3495 mA mg_{Pd}^{-1} which is much higher than that of 1539 mA mg_{Pd}^{-1} on Pd/MWCNTs electrode. The activities of the Ni@Pd/MWCNTs electrocatalyst were compared to others in literature. We found that the peak and mass current density of the Ni@Pd/MWCNTs is 1.4-20 times higher than the reported Pd/MWCNTs electrocatalysts [50,51], Ni-Pd alloy supported electrocatalysts [52,53], and Pd supported carbon and metal oxides electrocatalysts [54-57] at the similar electrochemical reaction conditions, displaying obvious commercial competition.

Moreover, the Ni@Pd/MWCNTs has about 80 mV negative onset potential than that on Pd/MWCNTs. The results indicated that the Ni@Pd core/shell and alloy structure significantly improved the activity and the output when used in fuel cells. This is extremely important for the efficiency of fuel cells. The above results were further evidenced by comparing the electrochemical active surface area (EASA) as shown in Fig. 4D. The EASAs of Ni@Pd/MWCNTs and Pd/MWCNTs were calculated according to the reduction region of PdO to Pd [58], they are 91.3 and $78.2 \text{ m}^2 \text{ g}^{-1}$, respectively. The EASA on Ni@Pd/MWCNTs is 1.2 times higher than that on Pd/MWCNTs, confirming that the core/shell catalyst could improve the use ratio of the Pt metal. However, the peak current density on Ni@Pd/MWCNTs is 2.3 times higher than that on Pd/MWCNTs. The times in EASA (1.2) is less than that in peak current density (2.3), indicating that the Ni has synergistic effect on Pd electrocatalyst. This result is consistent with the literature [58].

The chronopotentiometric testing was carried out as shown in Fig. 5. The results indicated that the Ni@Pd/MWCNTs electrocatalyst could sustain larger current densities for stable ethanol oxidation than that of Pd/MWCNTs electrocatalyst. The electrode potential was polarized to higher potentials at higher current densities than 10 mA cm⁻² on Ni@Pd/MWCNTs due to the loss of the catalytic activity for ethanol oxidation. However, the Pd/MWCNTs electrode could not sustain the constant current density of 6 mA cm⁻² due to the lower active surface area and lower utilization of Pd even at the same Pd loadings.

Based on the previous studies, the mechanism of ethanol oxidation on Pd electrocatalyst is described though the following Eqs. (1)-(5) [58–63]:

$$Pd + OH^- \rightarrow Pd-OH_{ads} + e^-$$
 (1)

$$Pd + CH_3CH_2OH \rightarrow Pd-(CH_3CH_2OH)_{ads}$$
(2)



Fig. 4. (A) Cyclic voltammograms of different alcohol oxidation on Ni@Pd/MWCNTs electrode, in $1.0 \mod dm^{-3}$ KOH/1.0 mol dm⁻³ alcohol solution at 303 K, scan rate: 50 mV s^{-1} ; (B) and (C) cyclic voltammograms of ethanol oxidation on Ni@Pd/MWCNTs and Pd/MWCNTs electrodes in $1.0 \mod dm^{-3}$ KOH/1.0 mol dm⁻³ ethanol solution at 303 K, scan rate: 50 mV s^{-1} and (D) cyclic voltammograms of Ni@Pd/MWCNTs and Pd/MWCNTs in $1.0 \mod dm^{-3}$ KOH/1.0 mol dm⁻³ to m^{-3} ethanol solution at 303 K, scan rate: 50 mV s^{-1} and (D) cyclic voltammograms of Ni@Pd/MWCNTs and Pd/MWCNTs in $1.0 \mod dm^{-3}$ KOH solution at 303 K, scan rate: 50 mV s^{-1} .

 $Pd-(CH_3CH_2OH)_{ads} + 3OH^- \rightarrow Pd-(CH_3CO)ads + 3H_2O + 3e^- (3)$

$$Pd-(CH_{3}CO)_{ads} + Pd-OH_{ads} \rightarrow Pd-CH_{3}COOH + Pd$$
(4)

$$Pd-CH_3COOH + OH^- \rightarrow Pd + CH_3COO^- + H_2O$$
(5)

So the final product would be the acetate. When the Ni was added to form the Ni–Pd alloy, according to Zhang's report [58], the Ni would transform to Ni(OH)₂ in alkaline media at the reaction



Fig. 5. Chronopotentiometric curves of ethanol oxidation on Ni@Pd/MWCNTs and Pd/MWCNTs at different current densities in 1.0 mol dm⁻³ ethanol/1.0 mol dm⁻³ KOH solution, 303 K.

potential and consequently increase the coverage of OH_{ads} on Pd surface, which would ultimately accelerate the reaction rate through the Eq. (6):

$$Pd-(CH_3CO)_{ads} + OH^{-Ni(OH)_2}Pd-CH_3COOH + e^{-}$$
(6)

Liang et al. [62] reported from the cyclic voltammetry studies that the rate determining step is the removal of the adsorbed acyl by the adsorbed hydroxyl, while the dissociative adsorption of ethanol proceeds quickly. Fang et al. [59] found that the catalytic performance of Pd electrode depend on the pH of the fuel solution. The best performance was observed in 1 M NaOH solution (pH = 14), while the electrochemical activity decreased by either increasing or decreasing the NaOH concentration. Spendelow and Wieckowski [64] attributed this "pH effect" to enhanced ion transport and facile charge transfer.

For the purpose of further comparing the kinetic and mass transport properties of the two electrodes, Tafel polarization analysis [58] and the relation between the peak current density and the scan rate [65] were provided. The Tafel plots are showed in Fig. 6A, the slopes for Ni@Pd/MWCNTs and Pd/MWCNTs electrocatalysts are 212 and 195 mV dec⁻¹ at 303 K, respectively. By extrapolating the Tafel line, to the point where the overpotential equals zero, the exchange current density can be obtained. The exchange current density for Ni@Pd/MWCNTs is 2.14×10^{-2} mA cm⁻², which is 4.7 times higher than that of Pd/MWCNTs (4.57×10^{-3} mA cm⁻²). The results indicate that the Ni@Pd/MWCNTs electrocatalyst is more efficient than the Pd/MWCNTs. The relation between the peak current density and the scan rate is showed in Fig. 6B. It is reported that the deflection from the linear line of the data at lower scan rates in the relationship of peak current density and square



Fig. 6. (A) Tafel plots of the Ni@Pd/MWCNTs and Pd/MWCNTs electrodes in 1.0 mol dm⁻³ ethanol/1.0 mol dm⁻³ KOH solution with a scan rate of 1 mVs⁻¹, 303 K and (B) plots of the peak current density against the square root of the scan rate for both electrodes.

root of scan rate on electrode indicates the improvement in the mass transfer [65]. The straight lines appear over the scan rate of 20 mV s^{-1} on both Ni@Pd/MWCNTs and Pd/MWCNTs electrodes. The results display that the ethanol electro-oxidation reaction on both Ni@Pd/MWCNTs and Pd/MWCNTs electrodes is kinetic controlled at low scan rate (>20 mV s⁻¹), and mass transport controlled at high scan rate (>20 mV s⁻¹).

There have been several interpretations about the improved catalytic activity and stability on the alloyed catalysts [66-68]. Firstly, it is approved that the catalytic activity is strongly affected by the catalyst surface structure [69,70]. The alloyed catalysts have different intermetallic surface structure or interaction comparing to the single metal catalysts, which will certainly affect the catalytic activity. Researchers called it electric "ligand effect" that between the two metal layers of the alloy catalyst, which could promote desorption of the toxic intermediate products such as CO [71] from the noble metal, and consequently improve the anodic catalyst activity and stability [72]. Secondly, the downshift in d-band energy center of the noble metal that induced by the presence of Fe, Co or Ni has been taken in account to interpret the unusual catalytic performance on the alloyed catalysts [73-75]. The thin layer of noble meta would become compressive in atom arrangement when supported on Fe, Co or Ni substrate. Hammer and Nørskov revealed that the narrow down of the d-band weakens CO adsorption because of decreased back-donation from Pt to anti-bonding CO orbitals [76]. Thus, the anodic catalyst activity and stability will be improved. Thirdly, the core/shell structure of the catalyst is also an important factor in improving the electrochemical activity, which results from the improvement in the use ratio of the noble metal due to its shell structure, as discussed in the "EASA" part.

To sum up, the ligand effect, downshift in d-band energy center and the core/shell structure may together promote the electrochemical activity and stability of Ni@Pd/MWCNTs comparing to Pd/MWCNTs.

4. Conclusions

A core/shell nanostructured Ni@Pd/MWCNTs was synthesized by impregnation-reduction method and replacement method and used as electrocatalyst for alcohol oxidation. The MWCNTs with surface being oxized made Ni-impregnated MWCNTs transformed into monocrystalline nickel nanoparticles at 600 °C under nitrogen atmosphere. Then Ni@Pd/MWCNTs nanosized catalysts were synthesized using replacement method. For ethanol oxidation, the Ni@Pd/MWCNTs showed 2.3 times peak current density as high as that on Pd/MWCNTs electrocatalyst at the same Pd loadings. The electrochemical results demonstrated that the electrocatalytic activity and stability of the Ni@Pd/MWCNTs composites for alcohol oxidation are significantly enhanced. This might be attributed to crystal nickel entered into palladium crystal lattice leading to synergistic effect. This also implies that Ni@Pd/MWCNTs may be good candidates for electrocatalyst because improving of the precious metal catalyst (Pd) effect in alcohol oxidation for fuel cells.

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