

Short communication

Vanadium oxide nanotubes as the support of Pd catalysts for methanol oxidation in alkaline solution

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Abstract

Well-dispersed Pd nanoparticles were prepared on the surface of vanadium oxide nanotubes (VO_x-NTs) through a simple reductive process. The morphology and structure of the resulting Pd/VO_x-NTs composites were characterized by transmission electron microscopy (TEM), electron diffraction (ED) and X-ray diffraction (XRD), the results showed Pd nanoparticles were well dispersed with the size distribution from 7 to 13 nm. The electrocatalytic properties of Pd/VO_x-NTs composites for methanol oxidation were investigated on the corresponding modified glassy carbon (GC) electrode in alkaline solution. The results indicated the prepared Pd/VO_x-NTs composites had an excellent electrocatalytic activity and stability.

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1. Introduction

In recent years, much attention has been attracted to the development of the methanol fuel cells (DMFCs), due to its important attributes such as quick refueling, low temperature and pressure operation, low cost of methanol, no liquid electrolyte, compact cell design, etc. [1,2]. Although much progress has been made in the power density and the fuel efficiency, a continuous effort is still necessary mainly in two aspects; one is the improvement of methanol oxidation catalyst, and another is the reduction of methanol crossover effect [3,4]. Recent work has been devoted to the research of more efficient catalysts; much interest was attracted to the modification of Pt, which was believed to be the best element for electrocatalysis [5–7]. However, Pt is costly and short supplied so that its applications were actually limited [8]. Recently, Pd-based catalysts have aroused intense interest due to its high catalytic activity and at least 50 times more abundance than Pt [9–11]. Methanol electrooxidation is a very complex process and dependent on many factors, such as the size and dispersion of the noble metal,

the properties of the supporting materials and the preparation methods [12–14]. Actually, a suitable supporting material plays a crucial role on the performance of the supported electrocatalysts owing to the interactions and surface reactivity [15,16]. Although there have been many reports available about carbon-supporting materials such as carbon nanotubes (CNTs) [17], porous carbon [18], carbon network [19] and so on, developing alternate electrode materials for better activity and stability for methanol electrooxidation is still in demand.

It has been proposed that transition metal bronzes were effective to remove the nascent hydrogen and the strongly adsorbed reaction intermediates from the Pt surface during dehydrogenation of methanol, and thus led to the performance the dehydrogenation over Pt at relatively low overpotentials [20,21]. Park et al. reported that the electrocatalytic enhancement of methanol oxidation at Pt-WO_x composite electrodes [22]. Rajesh et al. presented that the catalytic activity of Pt particles was greatly improved when PANI/V₂O₅ composites were employed as the supporting material [20].

The recently discovered vanadium oxide nanotubes (VO_x-NTs) are of particular interest because their morphology is associated with an intrinsic multifunctionality that arises from four different contact regions [23,24]. Compared with CNTs, VO_x-NTs were easily accessible as a pure product in gram quan-

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titities by low temperature hydrothermal synthesis, and had much higher reactive activity because of abundant defects on its surface [25]. In present work, we report on a facile method to prepare Pd nanoparticles supported on the surface of VO_x-NTs just by a simple reduction method. The electrocatalytic performance of the prepared Pd/VO_x-NTs composites was evaluated by methanol oxidation at the corresponding Pd/VO_x-NTs modified glassy carbon (GC) electrode. The results indicated that the as-obtained Pd/VO_x-NTs catalysts have an excellent electrocatalytic activity for methanol oxidation.

2. Experimental

2.1. Synthesis of VO_x-NTs

In a typical process, all chemical reagents are of analytical grade and used without further purification. VO_x-NTs were synthesized under hydrothermal conditions. V₂O₅ (0.909 g) and hexadecylamines (1.207 g) (C₁₆H₃₃NH₂) were mixed in 10 ml of ethanol. After stirring for about 2 h, 30 ml of deionized water was added dropwise to form a light orange suspension, and the mixture was continuously stirred for 48 h. The resultant system was then transferred into a Teflon-lined autoclave with a stainless steel shell. The hydrothermal reaction was processed at 180 °C for 7 days and then allowed to cool down to room temperature. The black precipitated was collected and washed several times with ethanol and hexane. The final product was dried in a vacuum at 80 °C for about 10 h.

2.2. Preparation of Pd/VO_x-NTs composites

0.1 g of VO_x-NTs was ultrasonic dispersed in 0.1% of PdCl₂ solution and stirred for 5 h. Formol was added to the system, and the reductive reaction was performed at room temperature for 10 h. The resulting composites were obtained and washed with deionized water and ethanol, and finally dried in a vacuum at 80 °C for about 5 h.

2.3. Fabrication of Pd/VO_x-NTs composites modified GC electrode

The GC electrode was firstly polished with chamois leather containing Al₂O₃ slurry, and then washed with deionized water and ethanol in an ultrasonic bath. Pd/VO_x-NTs composites were ultrasonically dispersed in 0.5% of Nafion ethanol solution. An aliquot of the Pd/VO_x-NTs/Nafion suspension was cast on the surface of the GC electrode and allowed to dry under an infrared heat lamp. The as-obtained Pd/VO_x-NTs modified GC electrode was employed as the working electrode in our experiments.

2.4. Apparatus

The morphology of the obtained composite was characterized by transmission electron microscope (TEM, Hitachi H-800) and X-ray diffraction (XRD, Cu K α , λ = 1.54178 Å, Rigaku D/MAX-2400). The electrochemical experiments were carried out with BAS-100 electrochemical analyzer (U.S.A.). A conven-

tional three-electrode system was used with a bare or modified GC electrode as working electrode (3 mm diameter), a Pt foil as counter electrode and a saturated calomel electrode (SCE) as reference electrode, respectively.

3. Results and discussion

3.1. TEM images of Pd/VO_x-NTs catalysts

Fig. 1a shows TEM images of Pd/VO_x-NTs composites. It was clearly observed that Pd nanoparticles were well dispersed on the wall of VO_x-NTs. The size distribution of Pd nanoparticles was in range from 7 to 13 nm by the TEM image analysis. Interestingly, there were much more Pd nanoparticles at the end of VO_x-NTs, and a slight aggregation was also found. We held the opinion that the aggregation may result from more defects at the end than those on the wall of VO_x-NTs. As is shown in Fig. 1b, the inner and outer diameter of VO_x-NTs was about 150 and 20 nm, respectively. To research the stability of VO_x-NTs in aqueous solution, the unmodified VO_x-NTs were dispersed in 1 M HCl and 1 M NaOH solution, respectively. VO_x-NTs dissolved completely in 1 M HCl after about 1 h; however, we found that the structure of VO_x-NTs had no changes in 1 M NaOH after the process of about 48 h (TEM images not shown here). It demonstrated that VO_x-NTs had a good alkaline tolerance. The ED patterns in Fig. 1c demonstrated the Pd nanoparticles were polycrystalline. According to previous reports, Pd particles were also obtained by using glycol as reductant above 120 °C [26]. However, we found that VO_x-NTs could be partially oxidized in open system at 120 °C. To keep the stability of VO_x-NTs, the stronger reductant, formal, was used in our experiments, and the reductive reaction can proceed at room temperature. Although the reaction with formal can be finished just in 1 h at higher temperature (such as above 80 °C), serious aggregation of Pd particles was formed. We suggested that the crystal nucleation was faster and the surface energy of crystal unit was higher at elevated temperature; the crystal particles therefore tended to aggregate in a short time. The case at low temperature was contrary to that at high temperature. Consequently, we optimized the reaction conditions as low temperature and relatively long reaction time (at room temperature for 10 h).

3.2. XRD analysis of Pd/VO_x-NTs composites

XRD patterns of Pd/VO_x-NTs composites are shown in Fig. 2. The peaks at 2.6°, 5.4° and 8.1° were attributed to (001), (002) and (003) diffraction of VO_x-NTs [23]. Furthermore, the major diffraction peaks of Pd nanoparticles can be clearly observed. According to Scherrer formula, the average size of the Pd nanoparticles was calculated to be 8 nm, which was consistent with the result of TEM images.

3.3. Electrochemical properties of Pd/VO_x-NTs composites

The electrocatalytic activity of Pd/VO_x-NTs composites were evaluated by the prepared Pd/VO_x-NTs modified GC electrode as working electrode in 1 M CH₃OH and 0.1 M NaOH solu-

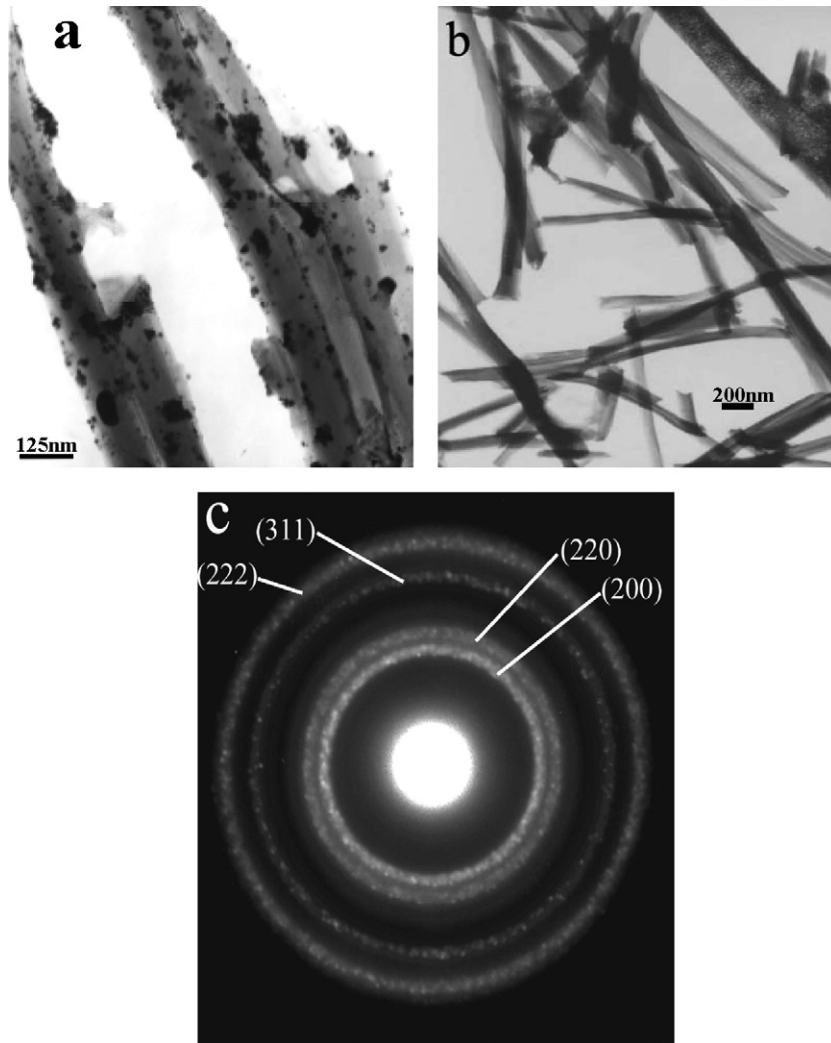


Fig. 1. (a) TEM images of Pd/VO_x-NTs composites, (b) TEM images of VO_x-NTs, and (c) ED patterns of Pd nanoparticles on the surface of VO_x-NTs.

tion. As is shown in Fig. 3a, two oxidation peaks are observed, which belong to the oxidation of methanol and the corresponding intermediates [27]. It is not the purpose of this paper to discuss the oxidation process in details, which has been described previously by others [28]. As we know, the voltage output of a

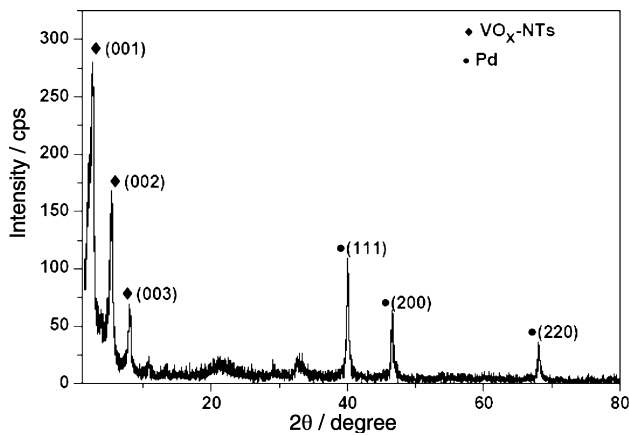


Fig. 2. XRD patterns of Pd/VO_x-NTs composites.

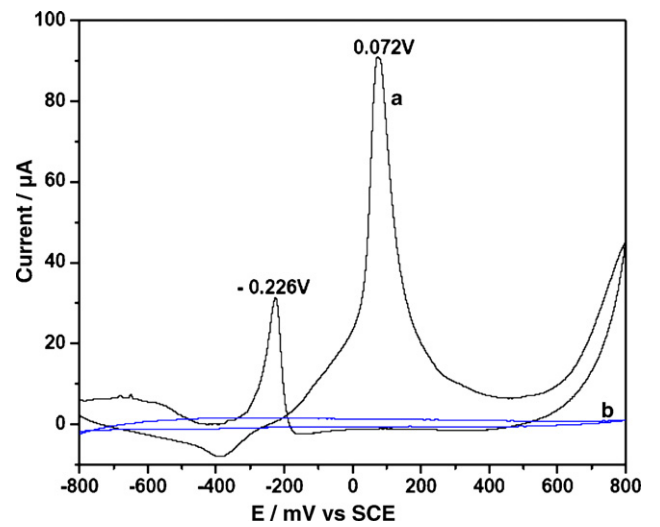


Fig. 3. Cyclic voltammograms of the oxidation of 1 M CH₃OH in 0.1 M NaOH: (a) Pd/VO_x-NTs composites modified GC electrode and (b) pure VO_x-NTs modified GC electrode; scan rate: 100 mV/s.

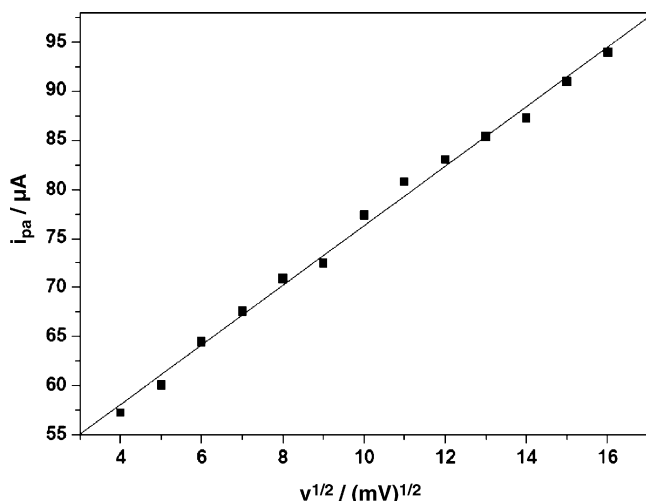


Fig. 4. Dependence of the peak currents on the square root of scan rates.

fuel cell at current density depends on the half cell potentials of both the anode and cathode; the more negative the anodic potential the higher the full cell voltage will be if the cathodic potential is fixed. Generally speaking, methanol is oxidized at potentials greater than 0.5 V in acid medium. As we expected, the oxidation potential of methanol was lowered to -0.226 V in our experiments based on Pd/VO_x-NTs composite catalysts in 0.1 M NaOH aqueous solution. Additionally, Pd nanoparticles were prepared at low temperature, and thus the chances of more defects are relative high; they may be assisted for the obtainment of high catalytic activity of Pd/VO_x-NTs composite catalysts. For comparison, the pure VO_x-NTs modified GC electrode was also researched under the same conditions. As is shown in Fig. 3b, the pure VO_x-NTs had hardly catalytic effect on the oxidation of methanol. The Pd/VO_x-NTs catalysts in present work can be therefore to be effective electrode catalyst for DMFCs.

Fig. 4 is a dependence curve of the peak currents on the square root of scan rates. The peak currents were linearly proportional to the square root of scan rates, which suggested the electrocatalytic oxidation methanol on Pd/VO_x-NTs was a diffusion controlled process [29,30].

The long-term stability of Pd/VO_x-NTs/GC electrode was investigated in 1 M CH₃OH and 0.1 M NaOH aqueous solution. As is shown in Fig. 5, the peak current decreases gradually with successive scans. The peak current of the 400th scan was about 82% of that of first scan. The loss of the peak current of methanol oxidation may result from the consumption of methanol during the long time for CV scans. Furthermore, it also may be due to poisoning and structure change of the nanoparticles as a result of perturbation of the potentials during the scanning in aqueous solutions, particularly in the presence of the intermediate organic compound during the methanol oxidation [27]. After the long term CV scans experiments, Pd/VO_x-NTs/GC electrode was immersed in deionized water for about 2 weeks; excellent catalytic activity of methanol oxidation was obtained when the experiments of methanol oxidation was performed again. It indi-

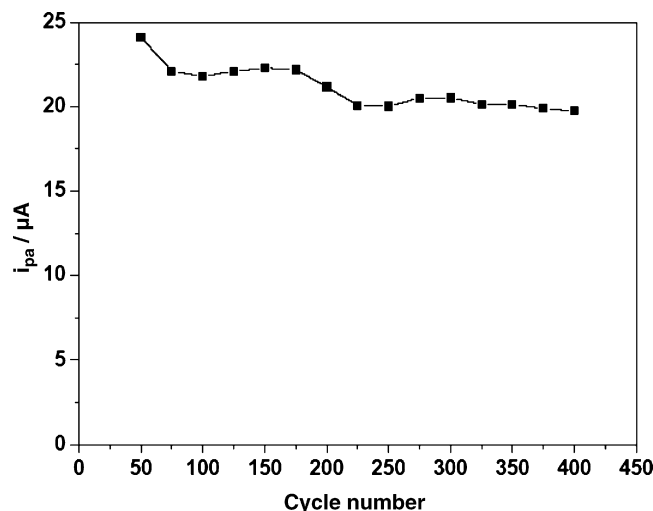


Fig. 5. Long-term stability of Pd/VO_x-NTs composites modified GC electrode in 1 M CH₃OH and 0.1 M NaOH aqueous solution; scan rate: 100 mV/s.

cates that the prepared Pd/VO_x-NTs composites have a good long-term stability and storage properties.

4. Conclusions

In summary, well-dispersed Pd nanoparticles supported by VO_x-NTs were successfully prepared through a simple reductive process. We first proposed that VO_x-NTs were used to act as catalyst supporting material. Compared with other supporting materials, VO_x-NTs can be easily synthesized as a pure product in gram quantities by low temperature hydrothermal synthesis and have much more reactive defects on their surface. The prepared Pd/VO_x-NTs composites showed an excellent electrocatalytic activity and long-term stability for methanol oxidation in alkaline media; it can be therefore applied in DMFCs as effective electrode catalyst.

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