Carbon nanotube/raspberry hollow Pd nanosphere hybrids for methanol, ethanol, and formic acid electro-oxidation in alkaline media

Zhelin Liu a,b, Bo Zhao c, Cunlan Guo a,b, Yujing Sun a,b, Yan Shi a,b, Haibin Yang c, Zhuang Li a,b,∗

a State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, PR China
b Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China
c State Key Laboratory of Superhard Materials, Jilin University, Changchun, Jilin 130012, PR China

A R T I C L E   I N F O

Article history:
Received 1 April 2010
Accepted 15 July 2010
Available online 18 July 2010

Keywords:
Carbon nanotube
Hollow Pd nanosphere
Fuel cell
Catalysis
Alkaline media

A B S T R A C T

In this paper, raspberry hollow Pd nanospheres (HPNs)-decorated carbon nanotube (CNT) was developed for electro-oxidation of methanol, ethanol, and formic acid in alkaline media. The electrocatalyst was fabricated simply by attaching HPNs onto the surface of CNT which had been functionalized by polymer wrapping. The as-prepared HPN–CNTs (CHPNs) were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS). The increasing interest and intensive research on fuel cell inspire us to investigate the electrocatalytic properties of the prepared nanostructures. Besides that, previous reports about alkaline other than acidic media could supply a more active environment guide us to examine the electrocatalytic properties in alkaline electrolyte. It is found that this novel hybrid electrocatalyst exhibits excellent electrocatalytic properties and can be further applied in fuel cells, catalysts, and sensors.

© 2010 Elsevier Inc. All rights reserved.

1. Introduction

In recent years, fuel cell has been receiving increasing attentions taking the advantages of high efficiency and cleaness. As alternative options, organic compounds such as methanol, ethanol, and formic acid have aroused lots of interest due to their high potential as fuel cell candidates. The electro-oxidation of these organic compounds has been intensively studied due to their potential applications in fuel cells [1–7]. With the development of nanotechnology, nanostructures offered new opportunities for searching and designing effective electrocatalysts, which have attracted the attention of many researchers and promoted the progress in this field. Among the exploited nanocatalyst, Pt-based catalyst has been considered as the best electrocatalyst in the low-temperature fuel cells [8], and many efforts have been made to design supported and unsupported Pt-based catalysts. However, the disadvantages of Pt, such as high cost and limited source, narrowed its use [9]. Thus, it is necessary to explore non-Pt catalysts to be applicable in direct-fueled cells. Some literatures have reported that alkaline media rather than acidic electrolyte could supply a more active environment to improve reaction kinetics, in which non-Pt catalysts could also be employed at the same time [10,11]. In recent years, Pt-based catalysts were found to be a good candidate of non-Pt catalysts, and they have been found to possess prominent electrocatalytic properties towards alcohol and formic acid [12–14]. In our previous work, hollow Au/Pd core/shell nanostucture with raspberry surface has been developed to electrocatalyse methanol, ethanol and formic acid in alkaline media [15]. Noble metallic nanostructure has attracted considerable attention due to its potential applications in many fields, such as catalysis, sensing, and SERS [16–19]. Since the catalytic property of nanomaterial crucially depends on its morphology, a great many efforts have been made on synthesizing nanomaterials with different morphologies. Hollow noble metal nanomaterials, which possess potentials for further cost savings, are arousing great interest recently [20,21]. The fabrication of hollow noble metallic nanostructures via a galvanic replacement reaction using cobalt nanoparticles as sacrificial template has been considered to be a facile and economic route [15,22–30]. However, the fabrications were usually carried out with N2 or H2 saturation in previous literatures, which made the experiment difficult to operate. Here, we fabricated hollow Pd nanospheres by a galvanic replacement reaction also involving Co nanoparticles as sacrificial template, but without the introduction of pure gas which has rarely been reported before [15,26]. The resulted hollow Pd nanospheres possessed a raspberry surface which might be helpful in increasing the surface area while applying as catalysts.

In recent years, carbon nanotubes (CNTs) have received noticeable interest due to their unique chemical and physical properties and potential applications [31]. It is desirable to obtain functionalized CNT-supported nanomaterial since it combines both the advantages
of CNT and nanomaterial which may be helpful in widening the applications, such as sensors [32], electrocatalysts in fuel cell [33], and single-electron transistors or memories [34]. In this study, PDDA was used to functionalize CNT, making the exterior wall positively charged. Then the negative-charged hollow Pd nanoparticles were attached onto the surface of the CNT by electrostatic interaction. This novel electrocatalyst was employed to investigate the electrochemical behaviors of oxidizing methanol, ethanol, and formic acid in alkaline media.

2. Materials and methods

2.1. Materials

Chemicals like cobalt chloride (CoCl₂·6H₂O), citric acid, sodium borohydride, palladium chloride (PdCl₂), nitric acid, hydrochloride acid, sodium chloride, poly(diallyldimethylammonium chloride) (PDDA), methanol, ethanol, formic acid, and potassium hydroxide were all of analytical grade and used as received without purification. Nafion (perfluorinated ion-exchange resin, 5 wt.% solution in a mixture of lower aliphatic alcohols and water) were purchased from Aldrich and used as received. Multiwalled carbon nanotubes (CNTs) were purchased from Shenzhen Nanotech. Port. Co. Ltd. (Shenzhen, China), and were purified and shortened by refluxing in 3 M HNO₃ for 24 h before functionalization. Ultrapure water (resistivity no less than 18 MΩ cm) was used throughout all experiments.

2.2. Preparation of hollow Pd nanospheres (HPNs)

HPNs were synthesized according to a simple galvanic replacement reaction previously reported with slight modifications [35]. Briefly, 0.01 g citric acid and 0.015 g NaBH₄ were added into a beaker containing 50 mL of water under vigorous stirring. Subsequently, 50 μL of 0.4 M CoCl₂ solution was injected into the above solution. Prior to synthesis, 56.4 mM H₂PdCl₄ solution was obtained by the following steps. 1 g PdCl₂ was dissolved in 36 mL of 0.2 M HCl aqueous solution and then diluted to 100 mL volume with water. When the solution ceased to bubble, 10 mL of water containing 500 μL of H₂PdCl₄ (56.4 mM) was added into the solution, changing the color of the solution gradually to black. The solution was stirred for another 30 min, and kept in ambient condition.

2.3. Synthesis of Pd nanoparticles

In this study, Pd nanoparticles were prepared according to a method previously reported [36]. In brief, a 50 mL mixture of aqueous H₂PdCl₄ (4.0 mM, 7.5 mL, 30 μmol of Pd), ethanol (10 mL), water (32.5 mL), and PVP (30 μmol) was heated at reflux temperature (100 °C) in a 100 mL flask for 3 h under air to synthesize the PVP-protected Pd nanoparticles.

2.4. Fabrication of CHPNs

Firstly, 50 mg CNT was added to 250 mL of 0.5 M NaCl aqueous solution containing 0.5 wt.% PDDA, and sonicated for 6 h. The solution was then centrifuged and washed with water in order to remove the excessive PDDA. Then, 2 mL of CNT and 8 mL of HPN solution were mixed together. After sonicated for 20 min, the mixture was stirred overnight to obtain the CHPNs. The product was centrifuged and concentrated.

2.5. Fabrication of different material modified glassy carbon electrode (GC electrode)

Desired amount of concentrated solution was pipetted onto GC electrode, and allowed to dry in air. Then 10 μL of 0.05 wt.% Nafion was casted onto GC electrode and dried under an infrared lamp, completing the fabrication of CNT, or Pd nanoparticle, or CHPN modified GC electrode.

2.6. Apparatus

The samples for TEM, SEM, EDX and XPS characterizations were prepared by placing certain amount of desired solution on a carbon-coated copper grid and silicon wafers respectively, followed by drying at room temperature. TEM images were recorded by a HITACHI H-7650 operated at an accelerating voltage of 200 kV. SEM and EDX data were obtained on a XL 30 ESEM FEG scanning electron microscope equipped with an energy-dispersive X-ray analyzer at an accelerating voltage of 20 kV. XPS measurement was performed on an ESCALAB-MKII spectrometer (United Kingdom) with Al Kα X-ray radiation as the X-ray source for excitation. All electrochemical experiments were carried out on a CHI 660A electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China), and conducted on a conventional three-electrode cell, which includes a platinum wire as counter electrode, a Ag/AgCl (saturated KCl) electrode as reference electrode, and a modified GC electrode (3 mm in diameter, purchased from Inner Mongolia University for the Nationalities) as working electrode. The cyclic voltammetric (CV) experiments for methanol or ethanol electro-oxidation experiments were carried out in 0.5 M KOH containing 0.5 M methanol or ethanol. For formic acid electro-oxidation, CVs were measured in 0.5 M KOH containing 0.5 M formic acid, and N₂ was bubbled for 20 min before the commencement of the experiments.

3. Results and discussion

Fig. 1 shows the schematic process of assembling hollow Pd nanospheres onto the surface of CNT. As is known, the unfunctionalized CNT cannot be well dispersed in aqueous solution, suggesting functionalization of CNT is necessary. In this study, the exterior wall of CNT was functionalized with PDDA with the aid of NaCl. In this way, the solubility of CNT in aqueous solution is enhanced and CNT is offered with positive charges. Meanwhile, HPNs were synthesized simply via a galvanic replacement reaction employing

Fig. 1. Schematic illustration of assembling HPNs onto the surface of CNTs.
Co nanoparticles as sacrificial template, and citric acid existed in solution supplied the as-prepared HPNs with negative charges. Therefore, when positively charged CNT and negatively charged HPNs were mixed and sonicated together, HPNs could be attached onto the surface of CNT by electrostatic interaction. The resulted CHPNs could be supported by the characterizations as followed.

TEM and SEM were employed to investigate the morphologies of the as-prepared nanostructures. Fig. 2a and d shows the typical TEM and SEM images of the prepared HPNs. It can be obviously seen that all nanospheres have a brighter center surrounded by much darker edges, indicating the existence of cavities. Besides that, the as-prepared HPN possesses a raspberry surface, and the average diameter of outside surface of the as-prepared HPNs was estimated to be 32 nm. Fig. 2b and e are the TEM and SEM images of CNTs. It can be seen that CNTs are in an average diameter of 50 nm. As discussed above, the as-prepared HPNs were offered with negative charges. When PDDA-functionalized CNT was added, negatively charged HPNs could be attached onto the positively charged surface of CNT by electrostatic interaction. Fig. 2c and f shows the typical TEM and SEM images of the prepared CHPNs. The images show that the structure attached on the surface of CNT is hollow nanosphere. The EDX data of HPN, CNT, and CHPN are shown in Fig. 2g–i. As shown in Fig. 2i, two main peaks assigned to C and Pd can be observed (the highest peak is ascribed to Si which comes from Si wafer). The chemical composition of the as-prepared CHPN was further characterized by XPS. Fig. 3a and b shows the Pd 3d (a) and C 1s (b) regions of XPS spectrum of CHPN. As shown in Fig. 3a, peaks at binding energies of 339.95 and 334.6 eV can be ascribed to Pd 3d_{3/2} and 3d_{5/2} respectively, which is in accordance with the data reported for metallic Pd [37]. From Fig. 3b, C 1s signal characteristic of CNT is also observed [38]. Combining the EDX and XPS data, the chemical composition of the hybrid material can be determined as C and Pd.

In order to investigate the electrochemical behavior of the as-prepared CHPNs, we applied this hybrid nanomaterial to be deposited on the surface of GC electrode followed by the deposition of Nafion. Fig. 4 shows CVs of CNT (a), Pd nanoparticle (b) and CHPN (c) modified GC electrodes in N_2-saturated 0.5 M KOH without...
adding any organic materials. The catalyst loading has been identified as 1 µg. It can be observed that no obvious response can be seen on CNT modified GC electrode (Fig. 4a), whereas Fig. 4b shows signals characteristic of Pd nanoparticles. In Fig. 4c, similar response to Fig. 4b is observed. This should be another support for successfully attaching HPNs onto the surface of CNT. The larger signal should be the contribution of the larger surface area increased by the 3D structure of CNT.

As is known, direct-methanol fuel cell (DMFC) has been attracting lots of attention in recent years. Sun et al. [13] have reported that covalent functionalized MWNT-supported Pd nanoparticles could be used for methanol oxidation in alkaline solution. Herein, the as-prepared CHPNs used as electrocatalyst for methanol oxidation in alkaline electrolyte were examined. Fig. 5 shows CVs of CNT (a), Pd nanoparticle (b), CHPN (c) modified GC electrodes in 0.5 M KOH containing 0.5 M methanol at the scan rate of 50 mV/s. As shown in Fig. 5c, two oxidation peaks can be obviously seen. One is an oxidation peak at about −0.160 V (vs. Ag/AgCl) in the forward scan, which is ascribed to the electro-oxidation of methanol. The other oxidation peak is at around −0.287 V (vs. Ag/AgCl) in the reverse scan, which is mainly assigned to the residual carbon species formed in the forward scan [39]. Similar electrochemical response can also be observed on Pd nanoparticle modified GC electrode (Fig. 5b), but is much lower than the signals obtained on CHPN modified GC electrode, indicating CHPN shows enhanced mass activity towards methanol oxidation than Pd nanoparticle. Besides that, CNT was also examined to investigate its electrochemical behavior for methanol oxidation. However, as shown in Fig. 5a, no obvious oxidation peaks can be observed comparing with the prepared hybrid structure. It can be concluded that the electrochemical signal for methanol oxidation obtained on the prepared hybrid nanostructures is higher than Pd nanoparticles and CNTs.

In recent years, ethanol used for fuel cell material has been arousing lots of notice due to its non-toxicity, natural availability, renewability, higher power density and zero green-house contribution to the atmosphere [2]. Thus, more and more efforts were made on the electro-oxidation of ethanol. Recently Pd-based catalysts has also been developed for ethanol electro-oxidation in alkaline electrolyte [12,15]. Xu et al. [12] have found that carbon microspheres supported Pd even shows excellently higher activity than Pt for ethanol electro-oxidation in alkaline media. Herein, we employed the as-prepared hybrid nanostructure as electrocatalyst to investigate its electrochemical behavior towards ethanol oxidation. Fig. 6 shows CVs of CNT (a), Pd nanoparticle (b), and CHPN (c) modified GC electrodes in 0.5 M KOH containing 0.5 M ethanol at the scan rate of 50 mV/s. As shown in Fig. 6c, the onset potential on the CV curve appears at around −0.550 V (vs. Ag/AgCl), a peak in forward scan is at about −0.191 V (vs. Ag/AgCl), whereas a peak in reverse scan is at about −0.288 V (vs. Ag/AgCl). Signals on Pd nanoparticle modified GC electrode shows similar but much lower peaks, suggesting the as-prepared hybrid nanostructure exhibits higher mass activity towards ethanol oxidation.
wards ethanol electro-oxidation which would increase the utilization of Pd and would help reduce the amount of noble metal used. Ethanol oxidation on CNT modified GC electrode was also examined and no obvious peak was observed. In this way, we can conclude that the as-prepared hybrid nanostructure exhibits excellent catalytic property for ethanol electro-oxidation. Experiments on methanol and ethanol oxidation discussed above also reveal that the prominent catalytic properties of prepared hybrid nanostructure can promote this new electrocatalyst to be applicable in DFCs.

Besides alcohol oxidation, Pd-based catalysts are also found to possess outstanding performances in oxidizing formic acid. Taking the advantages of easy availability, low cost, and low toxicity, formic acid is considered to be an excellent fuel alternative for methanol. Previous literatures have reported that carbon supported Pd catalysts usually show well-defined performance in acidic electrolyte [3–5]. However, few research has been carried out in alkaline electrolyte [15]. Fig. 7 shows the CV curves of CNT (a), Pd nanoparticle (b), and CHPN (c) modified GC electrodes in 0.5 M KOH containing 0.5 M formic acid. Scan rate: 50 mV/s.

Fig. 6. CVs of CNT (a), Pd nanoparticle (b), and CHPN (c) modified GC electrode in 0.5 M KOH containing 0.5 M ethanol. Scan rate: 50 mV/s.

Ethanol oxidation on CNT modified GC electrode was also investigated to make the comparison. However, comparing the as-prepared hybrid nanostructure, the peaks are hard to distinguish.

Furthermore, the electrochemical properties were also examined by varying the scan rates (data not shown). It is found that the current densities were all increased with the increment of scan rates in three solutions. Furthermore, the plots of current density towards the square root of scan rates were all in a linear relationship. In addition, the catalytic activity of the prepared hybrids was also compared with the commercial E-TEK Pd/C (purchased from Alfa Aesar), and the signals of our product were about two times higher than the commercial ones (data not shown). The chronoamperometric measurement was also applied to further investigate the electrochemical performance of the prepared hybrids, and showed good stability towards the three solution.

In summary, the prepared CHPN can exhibit excellent activity towards formic acid electro-oxidation. The excellent activity should be ascribed to the following reasons. First, 3D structure of CNT enlarged the surface of GC electrode. Besides that, the surface-to-volume ratio increased by the raspberry surface and the hollow cavity of the attached nanospheres further makes the electrocatalyst more efficient.

4. Conclusions

Electro-oxidation of methanol, ethanol and formic acid attracted lots of attention due to their potential applications in recent years. Carbon nanotube-supported hollow Pd nanospheres were developed as a novel electrocatalyst for methanol, ethanol and formic acid electro-oxidation in this study. The negatively charged hollow Pd nanospheres were attached onto the positively charged surface of carbon nanotube. The electrochemical results showed that the as-prepared hybrid nanostructure possessed excellent activities for oxidizing methanol, ethanol, and formic acid. This may be the contribution of 3D structure of carbon nanotube and the raspberry surface and the hollow cavity of Pd nanospheres.

Acknowledgments

Financial support by the National Natural Science Foundation of China (20775077), the National Basic Research Program of China (973 Program, No. 2010CB933600), and the Chinese Academy of Sciences (KJCX2-YW-H11) is gratefully acknowledged.

References