Applied Surface Science 268 (2013) 425–431

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Preparation of Pt nanoparticles on different carbonaceous structure and their applications to methanol electro-oxidation

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ARTICLE INFO

Article history:
Received 17 September 2012
Received in revised form
27 November 2012
Accepted 21 December 2012
Available online 29 December 2012

Keywords:
Direct methanol fuel cell (DMFC)
Graphene oxide (GO)
Methanol electro-oxidation

ABSTRACT

The efficiency of the direct methanol fuel cell (DMFC) is related to the dispersion of the metal catalyst on the support as electrode. It is important for the support to possess a high surface area, uniform pore size, and good conductivity properties. Graphene oxide (GO) is a newly developed 2-dimension material containing those excellent properties. The physical properties and structural information of the Pt/GO catalysts were further characterized by XRD, TEM, and XPS techniques. The TEM and XRD have revealed that the Pt/GO electrode catalyst prepared by polyol process possess a uniform dispersion and particle size within the range of 2–3 nm. The electrocatalytic properties of Pt/GO composites and kinetic characterization for methanol electro-oxidation were investigated by cyclic voltammetry. In addition, the Pt/GO shows better tolerance to CO for methanol electro-oxidation compared to the Pt/CNT catalyst. The results suggest that the Pt/GO catalyst as electrode has a good potential for application in DMFC.

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1. Introduction

Direct methanol fuel cells (DMFCs) have been studied extensively in the past decade because of their great potential for applications as renewable power sources [1–5]. DMFCs can be operated at low temperatures, have a high energy density, have long lives, are lightweight, and have simple system designs. Although DMFCs possess many advantages as power sources, their practical commercialization still faces several fundamental material challenges [3]. The basic construction of a DMFC involves methanol oxidation at the anode and oxygen reduction at the cathode [4]. The key issues to be addressed if DMFCs are to be commercialized are as follows: (1) the sluggish kinetics of methanol oxidation and (2) catalyst performance degradation resulting from methanol crossover. Investigations of DMFC technology dealing with electrocatalysts are mainly focused on developing more catalysts for oxygen reduction. Highly dispersed Pt has been widely investigated as an electrocatalyst for oxygen reduction for DMFCs [6,7]. It is essential and challenging work to prepare well-dispersed and uniformly sized metal particles for high performance catalysts in DMFC applications.

Catalytic performance depends on the catalyst supports, different active phases, and preparation methods. Regarding the effects of supports in catalytic activity, Lu et al. [8] and Dai et al. [9] have reported that significant treatment to the support can allow the active site to be dispersed well throughout the surface of the support and exhibit nano-scaled size. In addition, compared with other supports, carbonaceous materials have considerable advantages [10], such as high conductivity, high specific surface area, stability in acidic or basic media, and excellent mechanical strength. The conventional electrodes almost always use carbonaceous materials as supports [11], such as carbon black [12], carbon nanofiber [13], ordered activated carbon [14], and carbon nanotubes (CNTs) [15]. In particular, CNT have been extensively studied as supports for the dispersion of precious metal nanoparticles (NPs) to enhance electrocatalytic activity in fuel cells [16,17].

CNTs have received a great deal of research interest since. Their special characteristics such as 1-dimensional nanoscaled hollow cores, high surface area, excellent mechanical properties, high thermal stability as well as electron conductivity and good chemical stability. CNTs have been widely utilized as catalyst supports; however, there are still some limitations and drawbacks that need to be resolved [18–21], such as the problem that highly graphitized tube walls are generally hydrophobic, inert, and do not have enough binding sites to anchor Pt NPs, which leads to poorly dispersed and large-sized Pt NPs.

Graphene oxide (GO), one of the most important derivatives of graphene, is characterized by a 2-dimension structure with oxygen functional groups bearing on the basal planes and edges. Currently, GO is receiving considerable attention as a catalyst support for heterogeneous catalytic reactions [22,23] because of its uniform nanostructure, electrical properties, thermal stability, and abundant functional groups on its surfaces [24–26]. These surface sites are composed of carboxylic groups or hydroxyl groups that can act as nucleation centers for metal ions during the reduction [27]. The special properties of high electron conductivity and specific

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0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2012.12.115

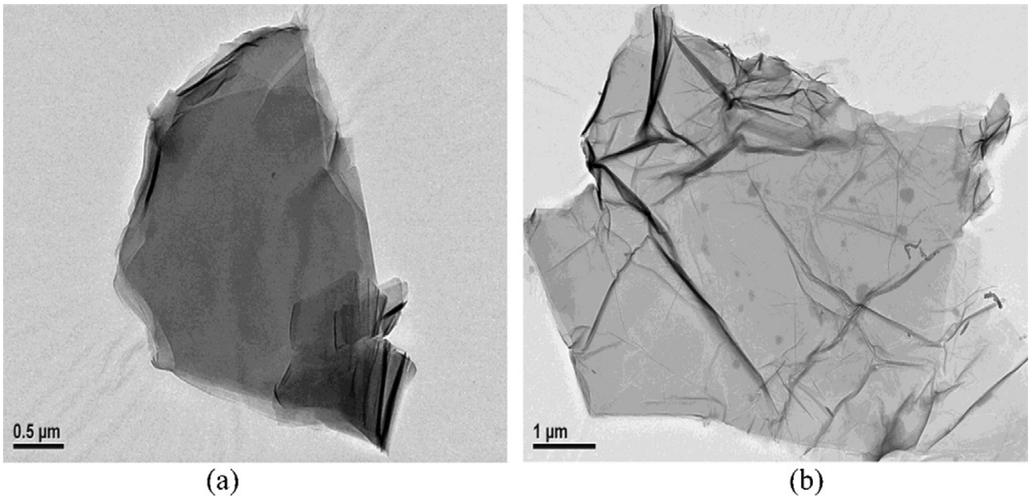

Fig. 1. TEM images of the (a) original graphite and (b) GO (upon oxidation/exfoliation of original graphite with strong acids).

surface area show the well potential application of GO for electrode material. GO has a good potential for improving efficiency of electrochemical catalyst layer in direct methanol fuel cell (DMFC) system.

In this study, the Pt/GO and Pt/CNT catalysts have been prepared by a polyol process from an ethylene glycol solution of Pt[$(NH_3)_4$]$(NO_3)_2$ as a precursor. The catalysts have been characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) in order to investigate the dispersion and particle sizes of the Pt NPs. The electrocatalytic activities for methanol oxidation for these materials were investigated with cyclic voltammetry.

2. Experimental

2.1. Materials and preparations

GO was prepared from purified natural graphite by the method reported by Hummers and Offeman [28]. The CNT were synthesized by the thermal chemical vapor deposition (TCVD) method with catalytic decomposition of methane [29]. The Pt/GO catalyst was prepared by a chemical reduction reaction of polyol process. A 0.04 g of the Pt[$(NH_3)_4$]$(NO_3)_2$ precursor (Strem Chemicals, 99%) was dissolved in 50 ml of ethylene glycol solution (Tedia, 99% purity). Then, a 125 mg of GO (CNT) was suspended in 150 ml of ethylene glycol solution and stirred with magnetic stir bar for 30 min. The above two solution chemicals were fully mixed with ultrasonic treatment for 10 min and refluxed at 180 °C for 6 h. The precipitated product was filtered and washed repeatedly with DI water at room temperature. The catalysts were air-dried at 100 °C in an oven for 1 h and the Pt loading was reached to 10% nominal content.

2.2. Characterization of the GO, Pt/GO and Pt/CNT

Particle size and powder morphology of the Pt/PCNT with different loadings were investigated using transmission electron microscopy (TEM, JOEL 1200-EXII) operated at 120 keV to observe the amorphous carbon and the dispersion of active sites on the support surface. The samples were suspended in alcohol. After ultrasonic dispersion, a droplet of the solution was deposited on a copper grid to form a perforated carbon film. The X-ray powder diffraction (XRD, SIEMENS, D-5000) instrument was used to identify the crystalline species of the Pt/PCNTs catalysts. A Cu tube serving as the X-ray source was employed to estimate the phase of the active site. The powder samples were pressed onto suitable holders. The scanning range of 2θ was from 20° to 80°. The scanning speed was 4°/min. Chemical composition of the Pt/PCNTs was determined by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, PHI 5000).

2.3. Electrochemical measurement

Cyclic voltarmmetry (CV) is the main way to discuss the electrochemical activity of electrode in the electrolyte solution. It shows potential values, current values and shaper to decide the electrochemical properties of electrode by cyclic oxidation/reduction scanning [30]. In this work, a conventional cell with three-electrode configuration was used the Pt/CNT or Pt/GO electrode was employed as working electrode. A platinum wire served as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. Electrochemical measurements were performed with ECW-5000 electrochemical workstation. The electrochemically active surface area was measured in 0.5 M H_2SO_4 aqueous solution at CV scan rate of 50 mV s^{-1}. The Methanol electro-oxidation test was measured in 0.5 M H_2SO_4 + 1 M CH_3OH aqueous solution at CV scan rate of 20, 50 and 100 mV s^{-1}.

3. Results and discussion

TEM images of the original graphite and GO are shown in Fig. 1. Fig. 1(b) shows the structural morphology of the GO characterized by TEM microscopy. It confirms the formation of GO with 2-dimension single-layered graphite after oxidation/exfoliation of the original graphite with strong acids.

The XRD patterns of the original graphite, GO, and reduced GO were shown in Fig. 2. The diffraction peak at $2\theta = 26.4°$ in the XRD pattern of graphite can be assigned to the (0 0 2) facets of the hexagonal crystalline graphite. Upon oxidation/exfoliation of original graphite with strong acids, the ordered the graphite layers was disrupted and a smaller, broader peak at $2\theta = 11.4°$ appeared for GO. Compared with pristine graphite, the disappearance of the peak at $2\theta = 26.4°$ and the appearance of the peak at $2\theta = 11.4°$ reveal the successful oxidation of the original graphite. After chemical reduction by a polyol process at 180 °C, the diffraction pattern

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