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Bucky diamond produced by annealing nanodiamond as a support of Pt electrocatalyst for methanol electrooxidation

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ABSTRACT

Bucky diamond (BD) with a nanoscale diamond core surrounded by a fullerene shell was used as a support of Pt electrocatalyst for methanol electrooxidation. BDs were prepared by annealing detonation-synthesized nanodiamond (ND) powders in 10^{-3} Pa vacuum at 900–1100 °C. The electrochemical properties of the BD powders in aqueous solution were investigated. The BDs and NDs supported platinum (Pt) electrocatalysts were prepared using a microwave-assisted reduction method. Higher dispersion of Pt nanoparticles was observed on the BDs than the pristine NDs, indicating a high affinity between BDs and Pt metal. The Pt/BD catalyst had better catalytic activity and higher stability for the methanol electrooxidation in comparison to the Pt/ND prepared at the same conditions. This provides a novel nanoparticle with a high conductivity and a high stability for electrochemical applications.

1. Introduction

Detonation-synthesized nanodiamond (ND) as a novel carbon material not only combines the unique properties of diamond such as extraordinary mechanical properties and chemical stability, but also possesses the features of nano-scale material such as ultrafine particle size and giant specific surface area as well as large numbers of surface functional groups [1,2]. Those features render it to be interested in numerous technological fields ranging from the use as tribological coatings to bio-interfaces. Several potential applications for ND, for example, biology [3–6], medicine [7–9], catalysis [10–12] have been reported.

Most recently ND powders consisting of diamond nanoparticles of ~5 nm have been incorporated into electrodes and biosensors [13–17]. ND is also promising for use as a Pt catalyst support for polymer electrolyte membrane fuel cells because of its enormous specific surface area and high thermal and chemical stabilities [18]. The primary role of the support is to provide a high surface area over which Pt nanoparticles can be highly dispersed and stabilized, which is necessary for catalysts to obtain a high catalytic performance and a high durability. Carbon materials are most popular support materials. However, sp^2-bonded carbon supports, such as activated carbon, carbon black, and graphitized carbons, are susceptible to corrosion and microstructural

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degradation during anodic polarization, which leads to a loss of activity due to catalyst detachment or even catastrophic electrode failure [19,20]. Novel nano carbon materials including carbon nanotubes, carbon nanofibers, graphene, and mesoporous carbon have been receiving attention for a long time as catalyst supports [21–27]. Compared with these commonly used sp^2-bonded carbon materials, sp^3-bonded diamond is highly resistant to electrochemical corrosion. So it is expected to be a more stable support [19,28–30]. We have electrodeposited Pt nanoparticles on ND support and confirmed the electrocatalytic effect on methanol oxidation [31]. Nevertheless, relatively low conductivity and electrochemical activity are obstacles for ND's use in electrochemical fields.

In order to improve ND's conductivity, we took a vacuum annealing treatment on ND powders in this study. Surface graphitization led to a formation of core-shell structural Bucky diamond (BD) with a nanoscale diamond core covered by a graphitic shell. This core-shell structure would endow ND a high conductivity and a high affinity with Pt catalyst metal, and also retain its high thermal stability. Moreover, the sp^2-bonded shell has a high affinity with Pt catalyst metal due to the interaction between the delocalized electrons of the graphitized layer and Pt d-electrons. This is a prerequisite for improving electrocatalytic activity of Pt catalyst. Therefore BD powder is thought to be suitable for use as a catalyst support for methanol oxidation. Pt nanoparticles were deposited on the surface of the BD powder using a microwave-assisted reduction method. As a rapid, uniform, and effective heating method, microwave heating has received considerable attention for nanosized materials synthesis. Pt supported on XC-72 carbon [32,33], CNTs [34–36], and graphene [37] have been prepared by microwave polyol process and show very good electrocatalytic properties for methanol electro-oxidation. The electrocatalytic effect of Pt catalysts supported on BDs and NDs for methanol electro-oxidation was studied.

2. Material and methods

ND powders with an average particle size of 5 nm were supplied by Element Six Ltd. The powders were heated up to 900–1100 °C respectively, for 1 h in 10^{-3} Pa vacuum, then cooled down to ambient temperature and drawn from the vacuum furnace to atmospheric air. Raman analysis, transmission electron microscopy (TEM), and electrochemical measurements were carried out before and after the annealing process.

Raman analysis was performed by a Renishaw inVia Raman microscope using the 514 nm line from an Ar ion laser. The phase structure was identified by means of X-ray diffraction (XRD). The measurements were carried out using a D/Max-2500pc diffractometer equipped with a standard Cu-Ka radiation source. The morphology was observed with a Hitachi H2120 transmission electron microscope.

All the electrochemical experiments were performed on a CHI660A electrochemistry analyzer. BD powders used in the electrochemical experiments were annealed at 1100 °C. Ten-milligram BD (or ND) powder was mixed with distilled water and Nafion (20% Nafion and 80% ethylene glycol) solution under sonicate for 20 min. One drop of the slurry was cast on a glass carbon (GC) electrode (2 cm in diameter) and dried at 80 °C to prepare the BD/GC (or ND/GC) electrode. A conventional three-electrode system was used, consisting of a BD/GC (or ND/GC) electrode as a working electrode, platinum coil auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode. Cyclic voltammograms (CVs) of the ND electrodes in 0.1 M KCl electrolytes and the solutions of 0.1 M KCl containing 0.01 M $Fe(CN)_6^{3-/4-}$ were recorded. The scan rate was set as 0.01–0.2 V/s.

Platinum precursor $H_2PtCl_6 \bullet 6H_2O$, ethylene glycol (EG), and H_2SO_4 were purchased from Shanghai Chemical Products Ltd. Deionized water was used to prepare the solutions and high-purity nitrogen gas was also used in the experiments.

Pt nanoparticles supported on BDs and NDs were prepared by microwave-assisted reduction. In a typical procedure, 4.0 ml of aqueous H_2PtCl_6 solution (0.055 M) was mixed with 25 ml of EG in a 100 ml beaker at room temperature (25 °C). The mixture was uniformly mixed with 40 mg BD (or ND) powder using ultrasound. The beaker was placed in the center of a microwave oven (Galanz G80F23CN3XL, 2450 MHz) and heated for 80 s at 800 W. The resulting suspension was filtered and the residue was washed with acetone and deionized water. The solid products were dried at 100 °C for 12 h in a vacuum oven. The prepared Pt/BDs and Pt/NDs were characterized by the methods of TEM and XRD analysis.

Pt catalyst modified GC electrode (Pt/BD/GC or Pt/ND/GC) was prepared using the same method as BD/GC electrode. CV curves in the supporting electrolyte of 0.5 M sulfuric acid (H_2SO_4) aqueous solution were recorded at the scan rate of 0.5 V/s. The methanol oxidation was studied in the same solution containing 1.0 M methanol. CV and CA curves were measured. In order to investigate the electrochemical oxidation of the supports, the CVs of BD/GC and ND/GC were measured between 0 and 1.2 V in 0.5 M H_2SO_4 for 500 cycles.

3. Results and discussion

Fig. 1 shows the Raman spectra of ND powder before and after vacuum annealing at the different temperatures. Raman

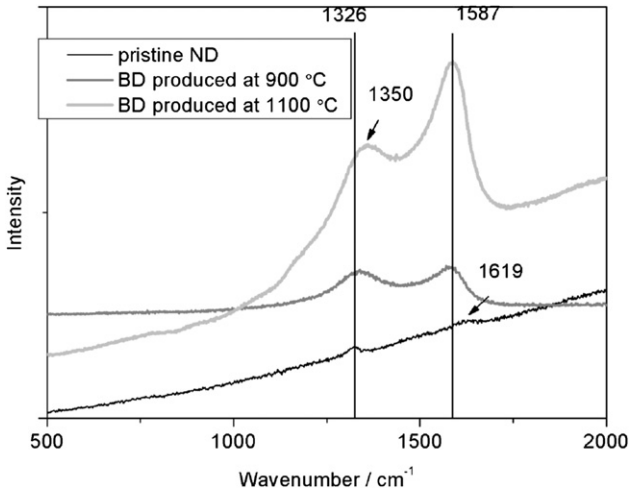

Fig. 1 – Raman spectra of the ND and the BD powders produced by vacuum annealing at 900 and 1100 °C for 1 h.