Materials Research Bulletin 60 (2014) 150–157

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Palladium nanoparticles anchored on graphene nanosheets: Methanol, ethanol oxidation reactions and their kinetic studies

D.H. Nagaraju [a,b,**], S. Devaraj [a,c], P. Balaya [a,d,*]

[a] Department of Mechanical Engineering, 117 576, Singapore
[b] Materials Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia
[c] School of Chemical & Biotechnology, SASTRA University, Thanjavur, 613 401, India
[d] Engineering Science Program, National University of Singapore, 117 576, Singapore

ARTICLE INFO

Article history:
Received 27 March 2013
Received in revised form 14 August 2014
Accepted 18 August 2014
Available online 21 August 2014

Keywords:
A. Metals
B. Chemical synthesis
A. Nanostructures
D. Catalytic properties
D. Electrochemical properties

ABSTRACT

Palladium nanoparticles decorated graphene (Gra/Pd nanocomposite) was synthesized by simultaneous chemical reduction of graphene oxide and palladium salt in a single step. The negatively charged graphene oxide (GO) facilitates uniform distribution of Pd^{2+} ions onto its surface. The subsequent reduction by hydrazine hydrate provides well dispersed Pd nanoparticles decorated graphene. Different amount of Pd nanoparticles on graphene was synthesized by changing the volume to weight ratio of GO to $PdCl_2$. X-ray diffraction studies showed FCC lattice of Pd with predominant (111) plane. SEM and TEM studies revealed that thin graphene nanosheets are decorated by Pd nanoparticles. Raman spectroscopic studies revealed the presence of graphene nanosheets. The electro-catalytic activity of Gra/Pd nanocomposites toward methanol and ethanol oxidation in alkaline medium was evaluated by cyclic voltammetric studies. 1:1 Gra/Pd nanocomposite exhibited good electro-catalytic activity and efficient electron transfer. The kinetics of electron transfer was studied using chronoamperometry. Improved electro-catalytic activity of 1:1 Gra/Pd nanocomposite toward alcohol oxidation makes it as a potential anode for the alcohol fuel cells.

1. Introduction

Direct alcohol fuel cells (DAFCs) are very attractive for portable electronic applications. However, the anodic catalytic oxidation of fuel remains a challenge for the commercialization of fuel cells. Metal and alloy nanoparticles have been used as the electro-catalyst for oxidation reactions in DAFCs [1–3]. Among various metal nanoparticles studied, Pt nanoparticle is known to show an excellent electro-catalytic activity toward alcohol oxidation reaction [4]. However, high cost of Pt and poisoning effect by reactive intermediates limit its usage in commercial applications. As an alternative to Pt metal, relatively less expensive Pd has been studied recently as a catalyst for alcohol oxidation reaction [5,6]. To reduce the cost of metal catalyst further, catalytic nanoparticles have been dispersed on the supporting materials, such as carbon, carbon nanotube, graphene and etc. Such a support not only decreases the catalyst loading and hence cost, it also increases the catalytic activity of the metal nanoparticles. The supported nanoparticles have also been used in many industrially important catalytic reactions [7].

Palladium nanoparticles having a high surface area-to-volume ratio have been used in various electrochemical reactions [8–17]. Several groups have studied the supported Pd as an electro-catalyst in alkaline medium. For e.g., Nagaraju et al. have studied the graphene decorated Pd nanoparticles (NPs) for ethanol oxidation reaction [6]. Pandey et al. have synthesized Pd nanostructure supported on polymer and investigated ethanol and formic acid electro-oxidation reactions [18,19]. Zheng et al. have studied the effect of support on the electro-catalytic activity of palladium [20]. To achieve high mass catalytic activity, Pd nanoparticles are also dispersed onto the carbon, carbon nanotubes [21–26]. To use as a fuel cell catalyst support, it should have a high surface area, good electrical conductivity and high stability.

The thinnest material in the universe, graphene is a two dimensional single layer of graphite sheet, which has attracted attention both from fundamental as well as applied research points of view. Graphene has sp^2-bonded carbon atoms with high surface area. Excellent electronic properties of graphene suggest that it

* Corresponding author at: National University of Singapore, Engineering Science Programme, Faculty of Engineering, Block E3A, #04-23 Engineering Drive, Singapore 117574, Singapore. Tel.: +65 65167644; fax.: +65 67754710.
** Corresponding author at: Department of Mechanical Engineering, 117 576, Singapore. Tel.: +65 65167644.
E-mail addresses: dhnagu@gmail.com (D.H. Nagaraju), mpepb@nus.edu.sg (P. Balaya).

http://dx.doi.org/10.1016/j.materresbull.2014.08.027
0025-5408/

may be incorporated as an electrode, making potential candidate as a building block unit for nanoscale devices. Graphene has been investigated for a variety of applications including microelectronic devices, batteries, supercapacitors, sensors, biomedicines, and mechanical resonators [27–29]. It is appropriate to study graphene as a support for metal nanoparticles in fuel cells application as it provides an option to decrease the loading of precious metal and hence the cost. Synthesis of graphene–Pt (Gra/Pt) nanocomposites and their application to fuel cells and sensors have been reported earlier [30–32]. However, there are only very reports on synthesis of graphene–Pd nanocomposites in the literature. For e.g., Hu et al. have synthesized the carbon nanosheet–Pd nanocomposites [33] and Hassan et al. have reported microwave assisted chemical route to synthesize graphene–metal nanoparticles [34]. Very recently several studies have reported on synthesis and catalytic application of Pd nanoparticles on graphene sheets [35–39].

In this article, we report the synthesis of Pd nanoparticles decorated graphene (henceforth referred as Gra/Pd nanocomposite) by simultaneous chemical reduction of graphene oxide and palladium salt. Different ratios of graphene to Pd nanoparticles were used in the synthesis. The electron transfer properties of Gra/Pd nanocomposite were studied using potassium ferrocyanide by cyclic voltammetry. The half peak potential also known as formal potential (an average of cathodic and anodic peak potentials) for the electron transfer at Gra/Pd nanocomposite and graphene is lesser compared to the stainless steel surface indicating that efficient electron transfer at the Gra/Pd nanocomposite and graphene surfaces. The electro-catalytic activity toward alcohols was studied in alkaline medium. Gra/Pd nanocomposite shows very good electro-catalytic activity. Tafel plot analyses show that (a) the methanol oxidation takes place via dehydrogenation reaction and (b) the ethanol oxidation is quite complicate.

2. Experimental

2.1. Synthesis of graphene oxide

All the chemical reagents used in this study were analytical grade (AR). Milli-Q water having a resistivity of 18 MΩ cm was used to prepare all aqueous solutions. Graphite oxide was synthesized according to the method reported by Hummers and Offmann [40]. In brief, graphite flakes (3 g) and $NaNO_3$ (1.5 g) were added to the concentrated H_2SO_4 (69 mL) and the mixture was cooled to 0 °C. To this mixture, $KMnO_4$ (9 g) was slowly added in small quantities and the temperature was maintained below 15 °C. Then the reaction temperature was slowly raised to 35 °C after it attained 35 °C, 138 mL of Milli-Q water was added into the reaction mixture. Followed by, the temperature of the reaction was increased to 98 °C, stirred for 15 min and cooled to room temperature. And then 3 mL of H_2O_2 was added and stirred continuously for another 30 min. The resultant solid was intensively washed with an aqueous 0.1 M HCl solution followed by distilled water. Thus obtained graphite oxide powder was sonicated in water (0.1 mg/mL) for 30 min to obtain graphene oxide.

2.2. One pot synthesis of Gra/Pd nanocomposite

Gra/Pd nanocomposite was synthesized in a single step. In a typical synthesis, 10 mg of palladium chloride was dissolved in 10 mL of graphene oxide solution (0.1 mg/mL) and stirred for 30 min. To this mixture, 100 μL of ammonia was added followed by 10 μL of hydrazine hydrate. Then the reaction mixture was heated to 60 °C for 30 min. The brown colored solution turned to black indicating a reduction process. After the reaction, the mixture was cooled to room temperature. The resulting solution was centrifuged; the product was washed several times with water and dried. Similarly graphene was synthesized without palladium precursor. Ammonia used in the synthesis disperses the graphene oxide very well due to the dissociation of protons of the functional groups of the graphene oxide and hence we could prepare dispersed Pd NPs on the reduced graphene using a reducing agent, hydrazine hydrate.

The synthesis of various amount of Pd was carried out by changing the weight percentage of palladium chloride by fixing the graphene oxide volume. The graphene oxide was obtained by dispersing 0.1 mg of graphite oxide in 1 mL of water. 10 mL of graphene oxide was used for the synthesis of Gra/Pd nanocomposite which corresponds to 1 mg of graphite oxide. Different ratios of graphene to Pd nanoparticles with a weight to weight ratio of 1:0.5, 1:1 and 1:2 were synthesized. The Pd contents in Gra/Pd nanocomposites were analyzed by inductively coupled plasma (ICP) Emission experiment conducted on the PerkinElmer Optima 5300 DV ICP-OES system. The Pd contents were found to be 80.8, 86.3 and 89.4 wt% respectively for 1:0.5, 1:1 and 1:2 (w/w) Gra/Pd nanocomposites. Low Pd contents obtained at high weight to

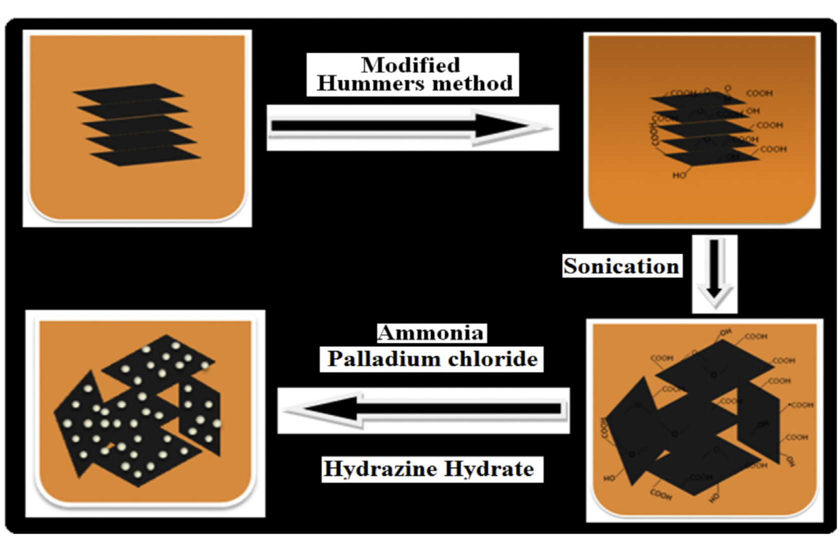

Fig. 1. Schematic representation of synthesis of Gra/Pd nanocomposite.