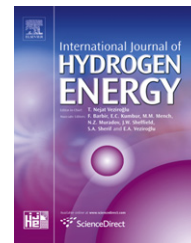


Available online at www.sciencedirect.com

SciVerse ScienceDirect

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

Facile synthesis of triangular shaped palladium nanoparticles decorated nitrogen doped graphene and their catalytic study for renewable energy applications

B.P. Vinayan^{a,b}, K. Sethupathi^b, S. Ramaprabhu^{a,*}

^a Alternative Energy and Nanotechnology Laboratory (AENL), Nano Functional Materials Technology Centre (NFMTC), Indian Institute of Technology Madras, Chennai 600036, India

^b Low Temperature Physics Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India

ARTICLE INFO

Article history:

Received 22 June 2012

Received in revised form

25 October 2012

Accepted 18 November 2012

Available online 3 January 2013

Keywords:

Nitrogen doped graphene

Triangular palladium nanoparticles

Hydrogen storage

Proton exchange membrane fuel cell

Oxygen reduction reaction

Methanol tolerance

ABSTRACT

We report a novel method for the synthesis of triangular shaped palladium nanoparticles (Pd NPs) decorated nitrogen doped graphene. Nitrogen doped graphene (N-G) is synthesized by uniform coating of polyelectrolyte modified graphene surface with a nitrogen containing polymer followed by their pyrolysis. The triangular shaped Pd NPs are decorated over nitrogen doped graphene (Pd/N-G) by kinetically controlling the polyol reduction process. The kinetic control of the growth of the nanoparticles and nitrogen doping of the supporting material leads to the formation of highly dispersed anisotropic nanoparticles over the graphene support. Hydrogen storage study of N-G and Pd/N-G give a storage capacity of 1.1 wt% and 1.9 wt%, respectively at 25 °C and 2 MPa hydrogen equilibrium pressure. Electrocatalytic study of Pd/N-G shows that it is a very good electrocatalyst for oxygen reduction reaction and highly stable in acidic media due to the strong binding between Pd NPs and graphene support as a result of nitrogen doping besides has high methanol tolerance in acidic media. The present synthesis procedure highlights a new pathway for the highly dispersed and different morphological metal nanoparticles decorated graphene composites for energy related applications.

Copyright © 2012, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Graphene, a single layer of graphite with carbon atoms arranged in a honeycomb lattice, has gained a lot of attention in scientific and technological fields because of its unique physical/chemical properties such as high surface area, excellent conductivity, mechanical strength and potential bulk quantity production along with low cost [1–3]. The

application of graphene in many fields such as energy storage materials, electrocatalysts, electronics, polymer composites and biosensors are well studied [2]. Theoretical and experimental studies have revealed that nitrogen and boron doping of graphene can modify the physical/chemical properties of graphene and can give new opportunities in the physics and chemistry of graphene [4–6]. Since chemically synthesized graphene usually suffers from the problem of low electrical

* Corresponding author. Tel.: +91 44 22574862; fax: +91 44 22570509, +91 44 22574852.

E-mail address: ramp@iitm.ac.in (S. Ramaprabhu).

conductivity, nitrogen doping can be used as a way to enhance the electrical properties. It has been well reported that nitrogen doping can tune the functionalized graphene from a p-type to n-type semiconductor [7].

Because of infuriating energy and environmental problems such as pollution, fossil fuel depletion and global warming it is necessary to find out clean and renewable energy materials as well as the designing of devices working with these renewable energy materials. The investigations of non-contaminating and renewable sources of energy give new promising fields of hydrogen energy and fuel cell technology [8]. The storage of hydrogen and its conversion to electric energy are the challenging tasks in the case of hydrogen energy. The large gravimetric and volumetric storage capacity, good reversibility, fast reaction kinetics and low cost are the necessary things required for a practical hydrogen storage media. In these aspects, carbon nanomaterials because of their light weight, high surface area and chemical stabilities are ideal materials for hydrogen storage applications [9]. The hydrogen storage properties of different carbon nanomaterials such as activated carbons, carbon nanofibers, carbon nanotubes and graphene have been studied in the recent past [9,10]. It has been well reported that dispersion of transition metals such as Pd, Pt, V and Ti over high surface area carbon materials can enhance the hydrogen storage capacity of these carbon materials by the catalytic activity of transition metals [11–13].

The high energy density, least corrosion problems, low operating temperatures and zero emissions make the proton exchange membrane fuel cells (PEMFCs) as a potential candidates for transportation and static applications [14]. The lethargic kinetics of oxygen reduction reaction (ORR) at the cathode of PEMFC causes a large over-potential and that reduces its performance to a great extent [15,16]. For the practical realization of PEMFCs, a highly active and durable cathode electrocatalyst must be developed at low cost with the replacement of present Pt-based electrocatalysts. Recent studies show that Pd-based catalysts can be used as cathode electrocatalysts in PEMFCs and its ORR activity is comparable with Pt-based electrocatalysts [17–19]. Since Pd is five times cheaper than Pt and electrochemically more stable than other 3d transition metals like Fe, Co and Ni, the incorporation of Pd nanoparticles on a large surface area and high electrical conductivity carbon support material can give a promising cathode electrocatalyst.

For the uniform dispersion of metal nanoparticles over graphene, the chemical modification of the inactive graphene surface is required. The present chemical modification like acid functionalization and plasma treatments can cause the destruction of novel properties of graphene like high surface area and excellent electrical conductivity etc. From this perspective, nitrogen doping is an efficient method for the attachment of metal nanoparticles without destructing the novel properties of graphene. Nitrogen doping of graphene can influence the growth kinetics of metal nanoparticles that lead to their small particle size, uniform dispersion, and different morphology [20]. Also, nitrogen doping of the support materials can give better chemical binding between support and metal nanoparticles resulting enhanced stability [21].

In the present work, nitrogen doped graphene was synthesized by the pyrolysis of polypyrrole coated polyelectrolyte functionalized graphene. The palladium nanoparticles were

dispersed over nitrogen doped graphene by modified polyol method and characterized by various techniques. The hydrogen storage properties of N-G and Pd/N-G have been investigated by the high-pressure Sievert's apparatus and the electrocatalytic activity of Pd/N-G and the performance of Pd/N-G as cathode catalyst in PEMFCs have been studied. The results depict that Pd/N-G have multifunctional properties in the field of energy.

2. Experimental section

2.1. Materials

The materials used in the present work are ethylene glycol (EG, Merck), sodium chloride (NaCl, Aldrich), poly(sodium 4-styrenesulfonate) (PSS, MW = 70 000, Aldrich), pyrrole monomer (Aldrich), hydrochloric acid (HCl, Aldrich), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Aldrich), palladium chloride (PdCl_2 , Aldrich), and Nafion solution (5% in isopropanol and water). Graphite oxide powder was used as-synthesized. Deionized (DI) water was used in all synthesis procedures.

2.2. Sample preparation

2.2.1. Synthesis of nitrogen doped graphene

Fig. 1 illustrates the scheme followed for the synthesis of the triangular shaped Pd nanoparticles decorated nitrogen doped graphene. Initially, graphite oxide (GO) was synthesized from graphite by Hummers' method [22]. Graphene was prepared from GO by hydrogen exfoliation method and the details have been explained elsewhere [23]. The as-synthesized graphene was functionalized with anionic polyelectrolyte PSS by the following procedure [15,24]. Initially graphene was dispersed by sonication in 1 wt% of PSS polyelectrolyte aqueous solution (0.15 mg mL^{-1}) and after the solution was stored at 50°C for 12 h. To take out the excess PSS, the final solution was filtered and then washed several times with DI water followed by drying in a vacuum oven at 70°C for 24 h.

After that, PSS modified graphene (PG) was uniformly covered with polypyrrole by chemical polymerization of pyrrole (0.5 ml) with an oxidizing agent FeCl_3 (1.2 g) in 0.1 M HCl solution. The remaining oxidants within the sample were removed by filtration and washing with a large amount of water and subsequently with ethanol. The final sample was again washed with acetone and dried at 60°C to obtain PPy-PG. During this procedure due to the strong electrostatic interaction between the negatively surface charged graphene and the positively charged PPy conducting polymer, a uniform coating of the nitrogen containing polymer (PPy) forms over the surface of graphene. Nitrogen doped graphene (N-G) was produced from PPy-PG sample by pyrolysis at 800°C in argon atmosphere. The pyrolysis of PPy-PG takes away the entire polymer from the graphene surface and dopes nitrogen atoms in the graphene network.

2.2.2. Synthesis of triangular shaped Pd nanoparticles decorated nitrogen doped graphene

Triangular shaped Pd nanoparticles were distributed over N-G by modified-polyol reduction method. For that, initially

Download English Version:

<https://daneshyari.com/en/article/1274087>

Download Persian Version:

<https://daneshyari.com/article/1274087>

[Daneshyari.com](https://daneshyari.com)