



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/ijhe](http://www.elsevier.com/locate/ijhe)

# Palladium nanoparticles supported on graphene as an efficient electrocatalyst for hydrogen evolution reaction

Shahram Ghasemi<sup>a,b,\*</sup>, Sayed Reza Hosseini<sup>b</sup>, Shima Nabipour<sup>b</sup>,  
Parvin Asen<sup>b</sup>

<sup>a</sup> Faculty of Chemistry, University of Mazandaran, Babolsar, Iran

<sup>b</sup> Nanochemistry Research Laboratory, Faculty of Chemistry, University of Mazandaran, 47416-95447 Babolsar, Iran

## ARTICLE INFO

### Article history:

Received 23 July 2015

Received in revised form

7 September 2015

Accepted 27 September 2015

Available online xxx

### Keywords:

Hydrogen evolution reaction

Dip coating

Pd nanoparticle

Graphene

Nanocomposite

## ABSTRACT

A nanocomposite with Pd nanoparticles deposited on graphene is prepared through a facile and low cost approach. The Pd-graphene nanocomposite was easily synthesized using dip coating method on glassy carbon electrode (GCE). The resulting Pd-graphene nanocomposite was characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). SEM indicates the formation of Pd nanoparticles with sizes in the range of 40–80 nm on graphene. Also, the behavior of as-prepared Pd-graphene nanocomposite as electrocatalyst for hydrogen evolution reaction (HER) was investigated by cyclic voltammetry in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Pd-graphene nanocomposite shows an enhanced catalytic activity toward HER than Pd and graphene. These results demonstrate that graphene is an excellent support material for Pd nanoparticles. It was observed that the current density of Pd-graphene nanocomposite had a little decrease after continues 500 cycling, which shows the catalyst presents high stability in the recycling process. Furthermore, the chronoamperometric method confirmed that the fabricated catalyst has good stability for HER. The good catalytic activity suggests that the Pd-graphene nanocomposite can be a promising electrocatalyst in hydrogen production process.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

With increasing energy demands and reduction of fossil fuel reserves, research on new environment-friendly energy sources has drawn great attention in the past decades [1]. Hydrogen is widely considered as one of the most promising power vectors because of its high energy conversion efficiency

and low pollutant emission which was powered by renewable energy sources such as water- or solar-based technologies [1–3]. Hydrogen generation from electrochemical splitting of water has attracted considerable attention because it is the simplest way to produce hydrogen with high purity at the most economical price [4,5]. Water electrolysis via hydrogen evolution reaction (HER) is promoted by efficient electrocatalysts which can generate hydrogen at room temperature.

\* Corresponding author. Nanochemistry Research Laboratory, Faculty of Chemistry, University of Mazandaran, 47416-95447 Babolsar, Iran. Tel.: +98 1135302397.

E-mail addresses: [sghasemimir@yahoo.com](mailto:sghasemimir@yahoo.com), [sghasemi@umz.ac.ir](mailto:sghasemi@umz.ac.ir) (S. Ghasemi).

<http://dx.doi.org/10.1016/j.ijhydene.2015.09.114>

0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Platinum (Pt) is regarded as the archetype of base metal for the electrocatalysis of HER in acidic media [6–8]. Unfortunately, its scarcity and high cost have hindered its commercial use in large scale [9]. In order to minimize the use of precious Pt, one of the efficient strategies is the loading of Pt on various carbon materials such as carbon black, carbon nanotubes, and graphene [10,11]. The most significant advantage is fewer amounts of catalyst loading and higher catalytic activity. Support materials have an important role in catalytic behavior of catalyst which is well known on performance of catalytic activity. Among carbon materials, graphene has been considered as an ideal support due to its exceptional properties, including large surface area and high electrical conductivity which causes improvement on ductility of the catalyst and increasing the dispersity of the active components [11–14]. These properties make graphene as a favorable catalyst support. However, Van der Waals attraction between graphene nanosheets reduces effective surface area of the graphene and thus the conductivity of graphene film decreases [15–17]. Xu et al. [10] synthesized Pt nanocuboids supported on reduced graphene oxide (RGO) as efficient electrocatalyst for HER. Pt-RGO hybrids exhibited higher catalytic activity and stability toward HER than Pt, which was attributed to the excellent conductivity of RGO and high dispersibility of Pt on RGO. Palladium (Pd), which is widespread in the earth crust and less expensive than Pt, is substitute for Pt as HER catalyst because of resemblance to Pt in many aspects such as excellent catalytic capability and hydrogen storage [18]. Unfortunately, the catalytic activity of Pd is lower than that of Pt [19,20]. Bimetallic alloys are more considerable for improvement of electrocatalytic performance of Pd catalysts [21]. Also, graphene-supported metal electrocatalysts (in particular electrocatalysts based on Pt and Pd) suggest a new class of catalysts, which show improved catalytic performance in fuel cells [22–24].

Attachment of nanoparticles on graphene is somewhat difficult. Therefore, it is crucial to choose a suitable chemical material as an adhesion agent. Proteins are complex amphiphilic biopolymers. Hydrophobic and hydrophilic patches on their surfaces make them well-known for their adhesiveness to graphene oxide surface and generate an extremely versatile and highly efficient self-assemble platform to construct graphene/noble metal composites [10,25].

L-Lysine was used to synthesize positively-charged cuboid-like Pt nanocrystals and then glued them on the negatively charged graphene oxide surface via electrostatic interaction [10]. Also, Qu's [26] group synthesized graphene oxide/Au nanohybrid through the self-assembly between graphene oxide and protein-stabilized Au nanoclusters. In this way, preparation of catalyst without the existence of any protective additives and significant stability is important for researchers.

In addition to the electrode materials, the preparation method is effective parameter on the performance of catalyst. Metal nanoparticles can be synthesized by using facile, inexpensive and conventional methods. To date, many methods have been developed such as electrochemical deposition [27,28], spontaneous deposition [29] and galvanic replacement [30,31]. Galvanostatic replacement is a facile and one step process which can be carried out without reducing agent. The deposition process of a metal from aqueous solution involves

both oxidation and reduction of two different metals/metal ions. Another method is dip coating, which is very similar to galvanic replacement. In this way, metal substitution doesn't occur on the electrode surface and it is simple, effective and low cost method to prepare metal nanoparticles on various substrates. An advantage of this procedure is the very low amount of metal required for the modification of electrode.

In this work, we used dip coating to prepare new nanocomposite based on graphene. The aim of using this procedure is the introduction of a new and facile approach to prepare Pd-graphene nanocomposite as promising catalyst in HER which can present larger current density at lower overpotential for HER. Up to now, there is no report on the use of Pd-graphene nanocomposite as electrocatalyst toward HER. Also, the electrochemical behavior of as-prepared nanocomposite was studied by cyclic voltammetry and electrochemical impedance spectroscopy (EIS) techniques.

## Experimental

### Materials and methods

Graphite powder,  $\text{NaNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$ ,  $\text{HCl}$  were purchased from Merck. Also,  $\text{PdCl}_2$  was purchased from Fluka.

### Instrumentation

The electrochemical experiments were carried out by using potentiostat/galvanostat Autolab (Nova software model PGSTAT 302N, Metrohm, Netherlands) electrochemical analyzer with three-electrode cell. Electrochemical impedance spectroscopy (EIS) was performed by potentiostat/galvanostat PalmSense (PSTrace software version 4.2.2, Netherlands). The three electrode system consists of the glassy carbon electrode (GCE) (diameter, 2 mm),  $\text{Ag}/\text{AgCl}/\text{KCl}$  (3 M) (the potential of  $\text{Ag}/\text{AgCl}/\text{KCl}$  (3 M) is 0.198 V vs. NHE; NHE represents the normal hydrogen electrode) and Pt wire as working, reference and auxiliary electrode, respectively. The surface morphology and elemental analysis were performed by field-emission scanning electron microscopy (FESEM, model MIRA3 Tescan) and energy dispersive spectrometer (EDS, VEGA-Tescan), respectively.

### Preparation of graphite oxide

Graphite oxide was synthesized by modified Hummer's method [32]. Firstly, 1 g of graphite and 1 g  $\text{NaNO}_3$  were suspended in 23 mL of concentrated  $\text{H}_2\text{SO}_4$  in a 1 L round-bottom flask under vigorous stirring. 4 g of  $\text{KMnO}_4$  was then added gradually with stirring and cooling so that the temperature of the mixture was maintained at 0 °C. The stirring was then continued for 1 h, followed by the addition of 180 mL of double-distilled water and stirring for another 15 min. Finally, the content of the flask was poured into 10 mL of 30% aqueous solution of  $\text{H}_2\text{O}_2$ . The resulting product was filtered by centrifugation and rinsed with 5%  $\text{HCl}$  solution and then washed several times with distilled water until the pH became neutral. The obtained product was dried at room temperature.

Download English Version:

<https://daneshyari.com/en/article/7713309>

Download Persian Version:

<https://daneshyari.com/article/7713309>

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