



# Facile fabrication of palladium-ionic liquids-nitrogen-doped graphene nanocomposites as enhanced electro-catalyst for ethanol oxidation



Shuwen Li <sup>a, b, \*</sup>, Honglei Yang <sup>a, b</sup>, Ren Ren <sup>a, b</sup>, Jianxin Ma <sup>a, b</sup>, Jun Jin <sup>a, b</sup>, Jiantai Ma <sup>a, b, \*</sup>

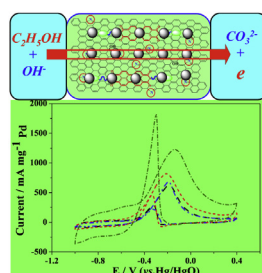
<sup>a</sup> State Key Laboratory of Applied Organic Chemistry (SKLAOC), College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

<sup>b</sup> Gansu Provincial Engineering Laboratory for Chemical Catalysis, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

## HIGHLIGHTS

- The palladium-ionic liquids-nitrogen-doped graphene catalyst is facile fabricated.
- The novel catalyst exhibits superior electrocatalytic performance for ethanol oxidation.
- The new catalyst is believed to have the potential use for DAFCs in the future.
- The functionalized NGS is promising useful materials applied in electro-catalytic fields.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 29 March 2015

Received in revised form

12 June 2015

Accepted 15 June 2015

Available online xxx

### Keywords:

Palladium nanoparticles

Ionic liquids

Nitrogen-doped graphene

Ethanol electrooxidation

## ABSTRACT

The palladium-ionic liquids-nitrogen-doped graphene nanocomposites are facile fabricated as enhanced electro-catalyst for ethanol oxidation. First, the ionic liquids functionalized nitrogen-doping graphene nanosheets (PDIL-NGS) with few layers is synthesized through a facile and effective one-pot hydrothermal method with graphene oxide as raw material, urea as reducing-doping agents and ionic liquids (ILs) derived from 3,4,9,10-perylene tetracarboxylic acid as functional molecules. The results of systematic characterization reveal that the PDIL molecules not only can functionalize NGS by  $\pi$ - $\pi$  stacking with no affecting the nitrogen doping but also prevent the agglomeration of NGS. More importantly, the processing performance and the property of electron transfer are remarkably enhanced duo to introducing a large number of ILs groups. Then, the enhanced electrocatalytic Pd nanoparticles are successfully anchored on PDIL-NGS by a facile and surfactant-free synthetic technique. As an anode catalyst, the novel catalyst exhibits better kinetics, more superior electrocatalytic performance, higher tolerance and electrochemical stability than the other catalysts toward ethanol electrooxidation, owing to the role of PDIL molecules. Therefore, the new catalyst is believed to have the potential use for direct alcohol fuel cells in the future and the functionalized NGS is promising useful materials applied in other fields.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

As a new promising kind of sustainable biomass-derived energy technology, direct alcohol fuel cells (DAFCs) based on liquid fuels have drawn a growing attention in recent years for portable power

\* Corresponding authors.

E-mail addresses: [lishw@lzu.edu.cn](mailto:lishw@lzu.edu.cn) (S. Li), [yanghl@lzu.edu.cn](mailto:yanghl@lzu.edu.cn) (H. Yang), [renr14@lzu.edu.cn](mailto:renr14@lzu.edu.cn) (R. Ren), [majx13@lzu.edu.cn](mailto:majx13@lzu.edu.cn) (J. Ma), [jinjun@lzu.edu.cn](mailto:jinjun@lzu.edu.cn) (J. Jin), [majiantai@lzu.edu.cn](mailto:majiantai@lzu.edu.cn) (J. Ma).

sources, electric vehicles and transportation applications, owing to the ever-increasing environmental problems and the up-coming depletion of fossil fuels [1,2]. Among all types of fuel cells, direct ethanol fuel cells (DEFCs) is a promising biomass-derived power sources and widely investigated due to its unique properties including higher theoretical mass energy density ( $8 \text{ kW h kg}^{-1}$ ), lower toxicity and operating temperature, easier in handling and transportation than other types of fuel cells [3–5]. Moreover, ethanol can be easily obtained on a large scale from chemical industry and fermentation of agricultural products or biomass [6]. In the development of DEFCs technology, the highly active electrocatalysts are important and necessary in order to completely oxidize each ethanol. Therefore, it has become a hot topic research to design and develop efficient ethanol electro-oxidation anode catalysts for DEFCs, especially in alkaline media [7]. Nowadays, the electrocatalysts of anode catalyst in DEFCs have predominantly relied on Pt based catalysts which have been extensively investigated [8–10]. Nevertheless, the commercialization of Pt based catalysts in DEFCs suffers from the intrinsic drawbacks of Pt based catalysts such as high cost, limited resource, susceptible to deactivation and vulnerability toward poisoning by intermediate products [11]. Recently, Pd-based nano-electrocatalysts are emerging as excellent substitute to Pt-based catalysts and have been proved to be a promising candidate for direct ethanol alkaline fuel cells (DEAFCs) because of more abundance, much cheaper, higher electrocatalytic activity and greater resistance to intermediate products for ethanol electro-oxidation in alkaline medium compared with Pt based catalysts [12–16]. However, there are also a number of challenges and obstacles for Pd based nano-electrocatalysts, such as poor catalytic activity and low utilization efficiency of Pd, which hinder the practical application in commercialization of portable fuel cell technology.

Besides the active metal regulation, another alternative effective approach to enhance electrocatalytic activity is to seek and develop novel catalyst supports such as ordered mesoporous carbons (OMCs) [17], Vulcan XC-72 carbon black [18], carbon nanofibers (CNFs) [19], carbon nanotubes (CNTs) [20], graphitized carbon materials [21], graphene [22] and nano-ceramic [23]. Moreover, it is necessary that the functionalization or stabilization of supports [24–27]. Graphene nanosheets (GS), as an atomic-layer-thick two-dimensional material, displays intriguing potential benefit as a support material for DEAFCs due to its many unique chemical and physical properties such as superior electrical conductivity, high surface-to-volume ratio, ultrathin thickness, structural flexibility and chemical stability [28]. To further tailor the catalytic support properties of GS, chemical doping is an important approach which has been proved effective in the doping of CNTs and greatly broadened their applications [29,30]. In particular, the nitrogen doping is important and perhaps the most frequently chosen method which can enhance the conductivity of GS and induces n-type semi-conductor behavior, because of the nitrogen atom is of comparable atomic size and contains five valence electrons available to form strong valence bonds with carbon atoms [31–34]. More importantly, the nitrogen doping graphene (NGS) with more functional groups for property design would be provided by the incorporating different types of nitrogen into the carbon network of GS [33,35]. Therefore, the combination of Pd nanoparticles (NPs) and NGS may open up a new avenue for designing the next generation catalysts for DEAFCs. Unfortunately, the synthesis approaches of NGS, including nitrogen plasma process, chemical vapor deposition (CVD), arc-discharge and hydrothermal reduction of graphene oxide (GO), are complicated, high-cost and suffer from difficulties in scaling up [33,36,37]. Presently, a simple hydrothermal reaction of GO and urea to prepared the high nitrogen level NGS was reported [36,37]. However, the NGS prepared by the above

method is easy irreversible aggregation and hard to disperse in aqueous solution which discourage its practical application in DEAFCs as electrocatalyst supports.

Aiming to design and develop efficient ethanol electrooxidation anode catalysts for DEAFCs, the present study combined with Pd NPs and ionic liquids functionalized NGS, fabricated a novel catalyst using a facile and environment-friendly approach. This work describes a facile and effective one-pot hydrothermal method with GO as raw material, urea as reducing-doping agents and ionic liquids (ILs) derived from 3,4,9,10-perylene tetracarboxylic acid (PDIL) as functional molecules to synthesize functionalized NGS. As a bifunctional molecule with an aromatic perylene group and ILs groups, the PDIL not only is a chemically inert molecule which does not affect the nitrogen doping but also can prevent the agglomeration of NGS. In addition, the PDIL molecules can functionalize NGS via  $\pi$ - $\pi$  stacking and introduced a large number of ILs groups, which can enhance the processing performance and electrocatalytic activity [16,38]. Then, the Pd NPs was anchored on the PDIL-NGS by a facile and surfactant-free synthetic technique. The morphology, structure, component and stability of PDIL molecules and as-prepared catalyst were investigated by systematic characterization. Furthermore, the as-prepared electrocatalysts were applied in DEAFCs and their electrocatalytic activity and durability was studied under half-cell conditions.

## 2. Experiment

### 2.1. Materials

The GO was synthesized by a modified Hummer's method [39,40]. All chemicals used for the synthesis could be purchased commercially without further purification. Water used in the experiments was deionized and doubly distilled.

### 2.2. Synthetic and preparation procedures

The PDIL was synthesized according to our previous reported literature and shown in [supplementary information \[41,42\]](#).

#### 2.2.1. NGS and PDIL-NGS

The GO (40 mg) were ultrasonicated in deionized water (30 mL) containing of PDIL (20 mg) for uniform dispersion. Then urea (1.2 g) was added into the above dispersion. After being vigorously stirred for 30 min, the mixture was sealed in a Teflon-lined autoclave (50 mL) and maintained at  $160 \text{ }^\circ\text{C}$  for 3 h. After that, the mixture was filtered through membrane and washed repeatedly with absolute ethyl alcohol and distilled water for several times. The final products were dried in vacuum oven at  $60 \text{ }^\circ\text{C}$  for overnight. A similar method was used to prepare the NGS. The only difference was that the PDIL was not added.

#### 2.2.2. Pd/NGS and Pd/PDIL-NGS

The PDIL-NGS (20 mg) or NGS (20 mg) was dissolved in  $\text{H}_2\text{O}$  (20 mL) with ultrasonic treatment to form a uniform suspension. Then,  $\text{K}_2\text{PdCl}_2$  solution (0.01 M, 4.7 mL) was added into the suspension under stirring and the mixture was stirred for 30 min in room temperature. Subsequently, the  $\text{NaBH}_4$  solution (8.4 mL 0.1 M) was delivered by drops into the above suspension under continuous stirring. After reacting for 4 h at room temperature, the black solid material was separated by centrifugation, washed repeatedly with water and ethanol several times, and finally dried in a vacuum at  $60 \text{ }^\circ\text{C}$  for 12 h. The Pd/RGO and Pd/C was prepared through the same method.

The fabricated route of the Pd/PDIL-NGS was summarized in [Fig. 1](#).

Download English Version:

<https://daneshyari.com/en/article/7730841>

Download Persian Version:

<https://daneshyari.com/article/7730841>

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