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Regular Article

Microwave-assisted synthesis of palladium nanoparticles intercalated nitrogen doped reduced graphene oxide and their electrocatalytic activity for direct-ethanol fuel cells

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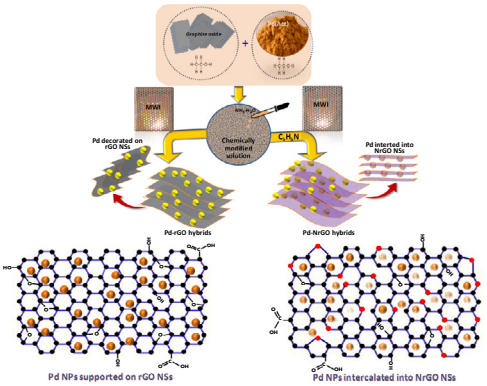
HIGHLIGHTS

- The simple and reliable strategy used to synthesize Pd-NrGO hybrid materials.
- Microwave approache help in reduction and exfoliation of graphite oxide.
- Insertion of Pd nanoparticles inside NrGO was found using microwave techniques.
- The Pd-NrGO have higher electro active surface area for ethanol electro-oxidation.

GRAPHICAL ABSTRACT

Schematic drawing of the mechanism responsible for the formation of Pd-rGO and Pd-NrGO hybrids.



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ABSTRACT

Palladium nanoparticles decorated reduced graphene oxide (Pd-rGO) and palladium nanoparticles intercalated inside nitrogen doped reduced graphene oxide (Pd-NrGO) hybrids have been synthesized by applying a very simple, fast and economic route using microwave-assisted in-situ reduction and exfoliation method. The Pd-NrGO hybrids materials show good activity as catalyst for ethanol electro oxidation for direct ethanol fuel cells (DEFCs) as compared to Pd-rGO hybrids. The enhanced direct ethanol fuel cell can serve as alternative to fossil fuels because it is renewable and environmentally-friendly with a high energy conversion efficiency and low pollutant emission. As proof of concept, the electrocatalytic activity of Pd-NrGO hybrid material was accessed by cyclic voltammetry in presence of ethanol to evaluate its applicability in direct-ethanol fuel cells (DEFCs). The Pd-NrGO catalyst presented higher electro active surface area (~6.3 $m^2 g^{-1}$) for ethanol electro-oxidation when compared to Pd-rGO hybrids

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($\sim$3.7 $m^2 g^{-1}$). Despite the smaller catalytic activity of Pd-NrGO, which was attributed to the lower exfoliation rate of this material in relation to the Pd-rGO, Pd-NrGO showed to be very promising and its catalytic activity can be further improved by tuning the synthesis parameters to increase the exfoliation rate.

1. Introduction

Due to the rapid industrial development with growing human population as well as pollution in present time and also depletion of fossil fuel reserves, there is needed and demand to generate new kind of environment-friendly and pollution free energy sources. So, for the synthesis of environment-friendly and pollution free energy sources have attracted tremendous attention around the world in the past few decades [1–4]. Thus it is necessary to synthesized low cost, high-performance and environmental-friendly materials using economic route for electrochemical energy conversion and its storage. The developments of high-performance anion-exchange membranes (AEM), there has been an increased interest toward various kind of electrochemical reactions for conversion and storage such as ethanol electro oxidation, hydrogen oxidation reactions and oxygen reduction reactions in AEM fuel cells (AEMFC). For this purpose, fuel cells are beneficial and required for promising electrochemical energy conversion and storage because a fuel cell is an electrochemical device that can convert the chemical energy of a fuel into electrical energy through chemical reactions on the interface of electrode and electrolyte. Also fuel cells are clean and environment-friendly energy source, have high energy conversion efficiency, has low pollutant emission, and has low operating temperature [5,6]. There are several kinds of fuel cells including polymer electrolyte membrane fuel cells (PEMFCs), direct methanol fuel cells (DMFCs), direct formic acid fuel cells (DFAFCs), direct ethanol/methanol fuel cells (DEFCs) etc., have been considered a class of the most promising power sources with high energy density and high efficiency [7–12]. Amongst above, DEFCs have been gaining a lot of attention due to their portability and easy handling, storage and transport because ethanol is non-toxic, renewable, and readily available. It also has higher energy density and lower crossover rate compared with methanol.

Graphene, an atomically thin carbon sheet with a hexagonal packed lattice structure, and its extraordinary properties makes it a promising candidate for many applications, such as batteries, supercapacitors, photovoltaic devices and fuel cells [13–16]. In these application, the most important and potential application of graphene is fuel cells [17–20]. The chemical exfoliation techniques used for larger scale and low-cost production of derivatives of graphene as graphene oxide nanosheets (GO NSs) and reduced graphene oxide nanosheets (rGO NSs). Significantly, GO NSs and rGO NSs produced by this approach possess lots of reactive oxygen-containing groups that provide many possibilities for further modification and functionalization. Doping of N in rGO NSs (NrGO NSs) is considered to be an excellent choice, because it has comparable atomic size with carbon and it forms strong bonds with carbon atoms and greatly used in fuel cells because of its enhanced conductivity, stability, and chemical activity [21,22]. In N-doped graphene (NG) or NrGO NSs, the lone electron pairs of N atoms can form a delocalised conjugated system with the sp^2-hybridised carbon frameworks, which improves the reactivity and electrocatalytic performance of graphene [20,23–25]. The role of doped reduced graphene oxide provides more support for catalysts in electrolyte membrane fuel cells and also related with different factors including (i) enhancement of high electroactive area, caused by a better dispersion of NPs [26]; (ii) improved electroactive species diffusion through the porous structure of rGO NSs support [26]; and (iii) promotion of the electronic transfer, either for the presence of surface functional groups or the shifting in Fermi level of the catalysts [27].

Currently, extensive studies have been focused on Pt or Pt-based hybrids catalysts due to its good electrocatalytic activity for ethanol oxidation [28,29]. However, the use of Pt-based hybrids electrocatalysts meant higher costs due to being expensive and as a substitute, Pd can be used which is cheap. Graphene has received considerable attention as an excellent supporting carbon-based material for Pd NPs. By decorating graphene with Pd NPs exhibits the enhanced performance with the obvious synergistic effects. Graphene-Pd NPs composites are proposed and exhibit superior electrocatalytic activities and high poison tolerance toward ethanol oxidation compared to other carbon-supported Pd [30–32]. The Pd NPs attached on the graphene surface have been synthesized by various strategies including electrochemical reduction, thermal reduction, and chemical reduction [30,31]. The graphene and its derivatives as GO NSs/rGO NSs decorated with different type of Pd nanostructures shows the various valuable applications as graphene-Pd for electrooxidation of formic acid [33], flower-like Pd nanoclusters on electrodeposited graphene electrode for hydrogen gas analysis [34], nanowall-like Pd-GO for electrochemical non-enzymatic sensor [35], Pd nanocubes-NG for electrochemical sensing [36], hollow and porous Pd nanospheres supported on rGO for H_2O_2 sensing [37], Pd-GO for catalytic reduction of 4-nitrophenol [38] etc. The Pd NPs supported on NG exhibited outstanding electrocatalytic performance than Pd/undoped graphene catalysts [38]. The N doping can not only induce anchoring sites for well dispersion of metallic NPs on the surface of graphene, but also modulate electronic property of graphene, thus directly affect the activity and the stability of metallic NPs during the electrocatalytic performance [39]. The NG can bring about high dispersity of metallic NPs, and the electronic effect between support and Pd NPs can be enhanced [40]. Besides doped graphene, the effect of doping on Pd NPs nucleation and growth is well documentated by several research groups reporting Pd NPs deposition by several methods on doped graphene [41], doped glassy carbon [42], doped HOPG [43], doped carbon nanotubes [44] and doped carbon [45,46]. The NG with Pd NPs shows more enhanced applications as methanol electro-oxidation [47,48], removal of halogenated emerging contaminants from water [49], formic acid and methanol oxidation [38,50,51], biosensor for methotrexate detection [52], oxygen reduction reaction [53] etc.

In this work, we report a simple and cost-effective approach as microwave assisted synthesis of Pd NPs decorated rGO NSs (Pd-rGO) and Pd NPs intercalated inside NrGO NSs (Pd-NrGO) hybrids materials as electrocatalytic activity for DEFCs. As illustrated in Fig. 1, graphite oxide synthesized by modified Staudenmaier's method and pyridine (C_5H_5N) as N precursor were first mixed together with graphite oxide in C_2H_5OH and sonicated for homogeneous dispersion. After removal of C_2H_5OH by heating, the chemically dried graphite oxide mixture was irradiated with microwave, which could allow the incorporation of N into the carbon skeletons of rGO NSs as well as the reduction and exfoliation of graphite oxide for the formation of highly porous structure. Subsequently, the as-obtained NrGO NSs could provide sufficient spaces/sites to