



Deoxyribonucleic acid directed metallization of platinum nanoparticles on graphite nanofibers as a durable oxygen reduction catalyst for polymer electrolyte fuel cells



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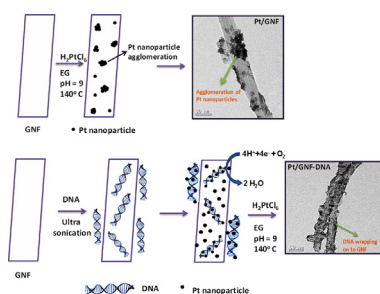
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HIGHLIGHTS

- GNFs are surface functionalized with a bio-polymer, DNA via π – π interactions.
- Pt nanoparticles of ~3 nm are uniformly deposited on to the GNF–DNA composite.
- Pt/GNF–DNA catalyst presented enhanced ORR activity and durability.
- Peak power density of 675 mW cm^{-2} is achieved with Pt/GNF–DNA in H_2 – O_2 PEFC.

GRAPHICAL ABSTRACT



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ABSTRACT

Effective surface functionalization to the hydrophobic graphite nanofibers (GNF) is performed with the biomolecule, namely deoxy-ribo-nucleic-acid (DNA) via π – π interactions. Pt nanoparticles are impregnated on GNF–DNA composite by ethylene glycol reduction method (Pt/GNF–DNA) and its effect on electro catalytic activity for oxygen reduction reaction (ORR) is systemically studied. Excellent dispersion of Pt nanoparticles over GNF–DNA surfaces with no evidence on particle aggregation is a remarkable achievement in this study. This result in higher electro chemical surface area of the catalyst, enhanced ORR behavior with significant enhancement in mass activity. The catalyst is validated in H_2 – O_2 polymer electrolyte fuel cell (PEFC) and a peak power density of 675 mW cm^{-2} is achieved at a load current density of 1320 mA cm^{-2} with a minimal catalyst loading of 0.1 mg cm^{-2} at a cell temperature of 70°C and 2 bar absolute pressure. Repeated potential cycling up to 10000 cycles in acidic media is also performed for this catalyst and found excellent stability with only 60 mV drop in the ORR half wave potential. The superior behavior of Pt/GNF–DNA catalyst is credited to the robust fibrous structure of GNF and its effective surface functionalization process via π – π interaction.

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1. Introduction

Polymer electrolyte fuel cell (PEFC) systems are intended to be used for transportation and portable applications mainly due to their low temperature operation and quick start-up. The slow and

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sluggish oxygen reduction reaction (ORR) on the cathode is a key reaction which limits the energy conversion efficiency of a PEFC [1]. Till date, Pt and Pt based alloy nanoparticles supported on high surface area carbon (Pt/C) represent the state-of-the-art electrocatalyst to catalyze the ORR with a high efficiency [2,3]. The efficiency of an electrocatalyst significantly depends on the particle size and dispersion of metal particles, on the carbon supports. Vulcan XC 72 R is widely used as a support material owing to its reasonably high surface area, good electronic conductivity. However, due to less graphitic character and poor electrochemical stability under acidic environment, Vulcan XC 72 R undergoes carbon corrosion resulting in agglomeration/detachment of the metal particles and hence reduces the catalytic activity [4]. To enhance stability of the support under PEFC environmental conditions, materials with higher graphitic nature such as carbon nanotubes, carbon nanofibers, graphene, and composites of carbon with transition metal oxides have been proposed in the literature for PEFC applications [5]. Among these, graphite nanofiber (GNF) is attractive because of its high degree of graphitic nature, unique fibrous structure and interaction of metal particles with GNF surfaces [6–8]. In addition, Pt nano particles supported on GNF surface will preferentially more accessible for ORR in relation to the Pt particles which are trapped in the micro-pores and geometrically restricted areas of carbon black support materials. However, intrinsic hydrophobic nature of GNF restricts its dispersion in polar solvents and as a result, uniform and wide dispersion of Pt nanoparticles over GNF is prohibited. To obviate the aforesaid issue, GNF needs surface activation prior to impregnation of Pt nanoparticles.

Generally, highly graphitic carbon materials are functionalized by either covalent bonding of functional groups directly to the π -conjugated system or non-covalent (π - π interaction) functionalization methods. Most universal covalent functionalization process is the acid oxidation which introduces surface-bound polar hydroxyl and carboxylic acid groups on to carbon support. However, the acid oxidation is inevitably accompanied with limitations, such as structural damage, loss in electrical conductivity and carbon corrosion due to highly oxidized carbon surface [9]. Hence, designing an effective functionalization method that can introduce high density and homogeneous functional groups which cause limited structural damage to the GNF is highly desirable [10–13]. Non covalent functionalization process includes adsorption of small organic molecules, such as 1-aminopyrene, benzyl mercaptan, 1-pyrenecarboxylic acid, and various functional polymers, like polyaniline, poly vinylpyrrolidone, poly (3,4-ethylene dioxy thiophene), poly (ethyleneimine), poly (diallyldimethylammonium) are also used to functionalize the graphitic carbon prior to impregnation of metal nanoparticles [14–22]. π - π interaction is a type of physisorption and an electrostatic interaction between molecules having π orbitals [23] which offers mild and effective functionalization to the carbon support without any structural damage preserving its inherent properties.

De-oxy-ribo-nucleic acid (DNA) is an appealing biomolecule used for templating inorganic nanostructures, for various applications such as synthesis of biomaterials, electronics and optical devices [24]. DNA possesses regularly arranged hydrophilic functional units such as phosphate groups and sugar molecules in a repeated fashion, is an effective dispersing agent to functionalize GNF surface and is interesting to study its effect on metal nanoparticles synthesis over the GNF–DNA composite. Besides, DNA is readily available and inexpensive biopolymer, which can act both as chelating and complexing agent to construct well defined hybrid nanostructures [25,26]. Hence, DNA plays a dual role, both as dispersing agent and complexing agent for the synthesis of well dispersed Pt nanoparticles on to the GNF surface.

The present study provides a facile method to surface

functionalize the GNF with DNA via π - π interactions which help in uniform deposition of Pt nanoparticles on GNF surface. Excellent dispersion of Pt nanoparticles over GNF–DNA surface with no evidence of aggregation is established, which is otherwise noted in case of Pt on pristine GNF surface. Pt/GNF–DNA catalyst exhibited better ORR behavior with a significant enhancement in mass activity. While evaluating this catalyst in PEFC, a peak power density of 675 mW cm⁻² at a load current density of 1320 mA cm⁻² is achieved at 70 °C and 2 bar absolute pressure, while the PEFCs with Pt/C and Pt/GNF catalyst delivers a peak power densities of only 561 mW cm⁻² and 548 mW cm⁻² respectively under similar operating conditions. Repeated potential cycling up to 10000 cycles in acidic media is also performed for Pt/GNF–DNA catalyst and found excellent stability with only 60 mV drop in the ORR half wave potential. High durability for Pt/GNF–DNA catalyst is due to the π - π interactions between GNF and DNA wherein DNA acts as a cross linker between GNF and Pt nanoparticles which prevents Pt surface diffusion and mitigate Pt aggregation with each other.

2. Experimental

2.1. Materials

Graphite nanofibers (GNF) (outer diameter 80–200 nm–inner diameter 0.5–10 nm, length 5–20 μ m) and DNA, were purchased from Sigma–Aldrich. Chloroplatinic acid, ethylene glycol (EG), ethanol, iso-propyl alcohol (IPA) were obtained from Acros Organics. Pt/C (40 wt % Pt on Vulcan XC-72 R carbon) was obtained from Alfa Aesar (Johnson Matthey Ltd.). All the chemicals were used as received. De-ionized water (18.4 M Ω cm) used for the experiments was produced by a Millipore system.

2.2. Surface functionalization of GNF and deposition of Pt nanoparticles

Surface functionalization of GNF with DNA was carried out similar to the process described elsewhere [24]. Briefly, 100 mg of GNF was suspended in 50 mL 1:1 volume ratio of methanol and water mixture containing 1.5 wt % of DNA and the mixture was ultrasonicated for 4 h followed by magnetic stirring overnight. The product was filtered and washed copiously with DI water to remove the free DNA and dried at 80 °C under vacuum for 12 h. The resultant GNF–DNA composite was used as catalyst support for impregnation of Pt nanoparticles.

Pt nanoparticles were deposited on pristine GNF and GNF–DNA composite by EG reduction method. GNF–DNA composite was suspended in EG solution and ultrasonicated to form an ink. Chloroplatinic acid dissolved in EG solution was added drop wise to the above ink under vigorous stirring for 2 h. The pH was adjusted to 9 by adding aqueous 0.5 M NaOH solution drop wise and the mixture was heated at 140 °C in an oil bath for 6 h for the complete reduction of Pt precursors. The product was filtered and washed copiously with DI water. The resulting Pt/GNF and Pt/GNF–DNA catalysts were dried at 80 °C under vacuum for 12 h. Pt loadings of ~22 wt % were achieved for all the catalysts.

2.3. Physico-chemical characterizations

The surface charge of the prepared catalysts was measured by dispersing the catalysts in IPA at a pH of 4.5 using zeta potential analyzer. The interaction of DNA with GNF and Pt precursor was monitored using UV–vis spectrophotometer. Powder X-ray diffraction (XRD) patterns for all the support materials with or without catalyst were obtained on a Philips Pan Analytical X-ray diffractometer employing CuK α radiation of wavelength 1.54 Å.

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