In-situ synthesis and characterization of metal free heteroatom doped graphene based oxygen reduction reaction catalyst from pyrolysed Assam silk cocoons

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Abstract: The fuel cell and electrolyzer together may be an important alternative source for clean energy production. The oxygen-hydrogen produced in the water splitting reaction in an electrolyzer may also be used in any conventional combustion engines with a little or no modification of the existing engines. The sluggish oxygen reduction reaction (ORR) in these devices necessitates higher loading of catalysts in the cathode. However, the best catalyst used in fuel cell and electrolyzer is platinum and/or its derivatives. The use of metal free graphene based heteroatom doped ORR catalyst may be a promising alternative for conventional platinum electrocatalyst. In particular, nitrogen-doped Graphene synthesized from natural carbon based biomass material has the potential to be a sustainable, green and economical ORR. In this study, Assam silk cocoons was used to synthesize nitrogen doped graphene based catalyst via one step in-situ pyrolysis. The morphological and chemical characterization of the synthesized catalyst was carried out with the help of XRD, Raman, FTIR, TEM, EDS and XPS. The X-Ray diffractograms of the catalyst revealed presence of defect induced broad peaks at graphitic 002 and 004 peaks at 24.5° and 43°, respectively. The Raman spectra showed the presence of D-band, G-band and D’ band with an ID/IG ratio of 0.86. The EDS analysis confirmed the presence of 21.55 At% in-situ nitrogen in the synthesized catalyst. The morphological analysis through TEM showed the presence of multilayer graphene. The formation of in-situ nitrogen doped graphene catalyst was confirmed through X-ray photoelectron spectroscopy, which showed the presence of pyridinic and graphitic nitrogen. The synthesized electrocatalyst was later analyzed with the help of a rotating disk electrode for its catalytic activity in ORR.

Keywords: Assam Silk, Doping, Electrocatalyst, Graphene, Pyrolysis, Oxygen Reduction Reaction

1. Introduction

Catalysts have been playing a vital role in the modern world of advanced power generation and storage technologies e.g. fuel cells and batteries [1]. Their use has revolutionized the electrochemical energy technologies to a great extent. The present scenario of such technologies uses either platinum (Pt) or platinum group metal catalysts to meet their demand for faster reaction rates [2]. Its use has made the electrochemical technologies reliable and capable for even higher power generation in the modern world. But high cost, sluggish kinetics towards oxygen reduction reaction (ORR), susceptibility to fuel crossover, and poor stability have restricted the use of Pt and Pt-based catalysts [3]. A catalyst which is more active, stable, sustainable and cost effective is the need of the hour for commercial viability of the fuel cell technologies. As a response for this demand, researchers and academicians have given more
attention on synthesis of carbon based catalysts. It has been repeatedly reported as a catalyst having properties such as high surface area, excellent conductivity, good stability, comparable catalytic activity etc. [4,5].

The carbon based catalysts have been developed in many forms, such as graphene, carbon nanotubes, carbon fibers, porous carbon nanosheets etc., depending upon their application[6]. Amongst these, graphene and doped graphene have evolved as the most active forms of carbon catalyst. Though graphene possesses extraordinary properties of high theoretical surface area (approximately 2630 m²/g), high thermal conductivity (5000 W/mK) high electrical conductivity (10⁶ S/m) high transparency (absorbance of 2.3%) and great mechanical strength (flexural strength of 42 N/m and Young’s modulus of 1 TPa), but lack of intrinsic bandgap and catalytic abilities have limited the application of pristine graphene [7]. With advancement in research and development it has been found that these disadvantages can be tailored by surface modification or chemical doping [8]. Thus heteroatoms such as nitrogen (N), boron (B), phosphorus (P), oxygen (O) and sulphur (S) are used as doping agents to create doped graphene. Doped graphene shows higher oxygen adsorption and provides more active sites in comparison to neat graphene [9,10]. Among all the non-metallic doped graphene, nitrogen doped graphene shows good electrical conductivity and more active sites [11,12]. But the conventional synthesis procedure of doped graphene electrocatalysts uses expensive and toxic dopants precursors, as well as it’s a tedious and time consuming procedure [13]. There is a scope for development of a simpler and cost effective synthesis technique using environmental friendly dopants and precursors.

In the present study, indigenously available Assam silk cocoon has been selected as a precursor for synthesis of graphene and nitrogen doped graphene (NG) catalyst. The silk material has economic value in the region and is commercially being used by handloom weavers for production of silk cloth. It is commonly known as Eri silk in the region. It has been reported that the cocoons of various types of silkworm possess fibrous structure, which is the fibroin enveloped by the glue-like sericin. These materials are known for their natural N-enriched carbonaceous materials [14]. The sericin covers the surface of these cocoons. Whereas proteinic fibroin contains 18 types of amino acids like glycine, alanine and serine, which account for 75% of the raw cocoons and contains organic nitrogen [15]. It is reported that the use of heat treatment on silk cocoons can transform them into sp² hybridized carbon hexagonal structure [16]. The synthesized catalyst was later characterized for its morphological, chemical, and electrochemical properties.

2. Methodology

2.1. Materials
The present study is conducted using silk cocoons obtained from the local village of Assam as a raw material. ACS reagent grade nitric acid was procured from Merck (make: Merck; product id: 438073) and used as cleaning agent along with double distilled water in all the experiments. Electrolyte for rotating disk electrode studies were prepared using reagent grade KOH (make: Merck; product id: 484016).

2.2. Synthesis of nitrogen doped graphene catalyst
The silk cocoons were pre-processed by reducing their size into smaller sections followed by boiling in distilled water for one hour. The boiled mixture was then rinsed and the fibrous materials were spread with the help of a glass spatula to enhance the net effective area. The fibrous dispersion was then filtered and the residual material was oven dried for 2-3 hours until complete removal of moisture. The sample is further pyrolyzed at 800°C for 5 hours under nitrogen environment and is grounded into fine powder. The grounded sample is ultra-sonicated at a frequency of 35 kHz for 2 hours. The resultant residue of the sample is then treated using nitric acid for 24 hours. After the treatment process the sample is thoroughly washed with distilled water till its pH becomes neutral. Further removal of moisture in the sample is done by oven drying it at 102°C for 12 hours. The obtained sample is further analyzed and is labeled as NG. Schematic illustration of the sample is shown in fig. 1.
Figure 1: Schematic illustration of the synthesis of NG from Assam silk cocoons

2.3. Characterization

The crystallographic analysis of the synthesized material was carried out with the help of XRD analyzer (make: BRUKER AXS, Germany; model: D8 FOCUS) using Cu-Kα radiation at 30kV and 450W, with a scan rate of 0.052 h/s. Similarly, identification of the dopant in the parent material was analyzed with the help of Raman Spectroscopy (make: FEI Company, USA; model: TECNAI G2 20 S-TWIN). Elemental mapping of the same sample was performed using the attached Energy Dispersive Spectrometer. The sample was further analyzed with the help of a FTIR spectrometer (make: Nicolet, USA; model: Impact 410). The doping of the sample was evaluated with the help of an X-ray Photoelectron Spectrometer (make: Kratos Analytical Ltd, UK; model: Kratos Axis Ultra DLD) with an aluminum (mono) Kα source (1486.6 eV). During the XPS study the Al-Kα source was operated at 15 kV and 10 mA. The raw silk cocoon was also analyzed with the help of an HCN analyzer (Make: Perkin Elmer; Model: 2400 CHNS/O Series II System) to determine its elemental composition.

The morphological analysis of the sample was carried out with the help of a Transmission Electron Microscope (make: FEI Company, USA; model: TECNAI G2 20 S-TWIN). The sample was further analyzed with the help of an X-ray Photoelectron Spectrometer (make: Perkin Elmer; Model: 2400 CHNS/O Series II System) to determine its elemental composition. The electrochemical analyses of the synthesized catalyst was carried out with the help of a potentiostat-galvanostat (make: Metrohm, Switzerland; model: AUT.RDE) setup (make: Metrohm, Switzerland; model: AUT.RDE)

3. Results and discussion

Preliminary study of the synthesized NG sample was carried out using an XRD analyzer and its diffractogram is shown in fig. 2(a). The broad peak at 2θ = 24.5° in the diffractogram corresponds to a d-spacing of around 0.362nm. This indicates a low degree of crystallization and/or indication of the stacking of graphene sheets. The low intensity nearly flat peak at 2θ = 43° is the graphite signature peak corresponding to 101 plane. It indicates that all the six carbon in the graphene are not sp² hybridized. Moreover a broad diffraction peak indicates possible encapsulation of nitrogen within the two dimensional graphene structure. The nitrogen may be a member of the closed ring during carbonization or may be associated with an edge carbon atom in the form of oxygen or nitrogen surface groups [17].

Figure 2: (a) X-Ray Diffractogram, (b) Raman, and (c) FTIR spectrographs of synthesized NG

The Raman spectrograph of the NG is shown in fig. 2(b). The peaks at 1376 cm⁻¹, 1607 cm⁻¹ and 1650 cm⁻¹ in the spectrograph correspond to the D-band, G-band and D’ band, respectively. The resultant D band is associated with the disorder arising from sp³ structural defects sites and is very weak for a single graphene sheet, but with increase in number of layers its intensity increases. The G band in an aromatic carbon signifies the phonon stretching mode of the sp²-bonded carbon. The ratio of the intensity
between D and G bands i.e. \( I_D/I_G \) could be used to identify the amount of defects in the sample. A larger ratio corresponds to larger defects introduced by heteroatom doping and/or a less sp\(^2\) electronic configuration. It has been found that the \( I_D/I_G \) ratio of NG is \( \sim 0.86 \). Literature shows that presence of disordered-induced peak indicates a weak D’ band at the shoulder of G peak, which is induced due to lattice disorder in the carbon \[18\]. Moreover presence of 2D band is sensitive to the number of layers and its position, the height indicates the layering in graphene \[19\]. A weak and low peak at 2780 cm\(^{-1}\) represents 2D band, which convinces that the sample contains highly disordered, randomly arranged and layered graphene. Energy Dispersive Spectrometer (EDS) shows that the sample NG contains 71.91 At\%, 21.55 At\% and 6.54 At\% of carbon, nitrogen and oxygen respectively. Thus, EDS analysis confirms the presence of nitrogen in sample NG, which is responsible for the defects discussed in XRD and Raman analysis.

The sample NG is further analyzed to detect the presence of functional groups using FTIR spectrum as shown in fig. 2(c). The interferogram shows a broad peak in the region 3000-3700 cm\(^{-1}\) due to presence of adsorbed H\(_2\)O molecules and N-H stretching. The peak at spectrum shows peaks at around 2930 cm\(^{-1}\) (CH), 1580 cm\(^{-1}\) (C=N), 1390 cm\(^{-1}\) (N-CH\(_3\)), 1270 cm\(^{-1}\) and 1000 cm\(^{-1}\) (C-N), 890 cm\(^{-1}\) and 740 cm\(^{-1}\) (substitute aromatic ring). Thus the FTIR analysis shows the presence of nitrogen in different functional groups of sample NG. Transmission electron microscope (TEM) analysis of sample NG shows the presence of single, stacked and disordered graphene sheets like structure with embedded amorphous mass shown in fig. 3.

![Figure 3: HRTEM micrograph of synthesized NG showing layers of doped graphene layers](image1)

![Figure 4: XPS spectrum of synthesized NG showing C1s, N1s and O1s at 285.30, 398.44 and 531.00 eV, respectively](image2)

X-ray photoelectron spectroscopy (XPS) analysis was performed to study the elemental analysis and bonding configuration of the synthesized NG. The XPS spectrum (fig. 4) shows three distinct peaks at around 285.30 eV, 398.44 eV and 531.00 eV corresponding to C 1s, N 1s and O 1s respectively. This reveals the presence of C, N and O confirming that the prepared material is indeed a nitrogen doped nanomaterial. Further in order to analyze the elemental compositions, high resolution spectra of C 1s, N 1s and O 1s are employed. The high resolution spectrum of C 1s reveals peaks at binding energies of 284.73 eV, 286.18 eV and 290.54 eV corresponding to C=C, C-N/C=O and C=N/C=O, respectively. The high resolution O 1s spectrum exhibits two major peaks at the binding energies of 532.23 eV and 533.33 eV corresponding to C-O and C-OH, respectively \[13\]. The high resolution N 1s spectrum was deconvoluted and four peaks were found at approximately 397.83, 398.46, 400.54 and 404.10 eV, which are assigned to pyridinic nitrogen, pyrrolic nitrogen, graphitic nitrogen (also termed as quaternary nitrogen) and oxidized nitrogen respectively. This indicates that the nitrogen present in amino group of the sample has transformed into pyridinic, pyrrolic and graphitic nitrogen during the process of carbonization. Literatures show that the presence of pyridinic and graphitic nitrogen in materials shows high catalytic activity. Thus the presence of pyridinic and graphitic nitrogen in the prepared sample as revealed by the XPS spectrum will facilitate the catalytic activity of the sample and benefits the ORR activity.
The synthesized NG catalyst was later analyzed with the help of an electrochemical analyzer in an RDE setup. Fig 5 shows the ORR performance of the synthesized N-doped graphene catalyst, synthesized from silk cocoon, on RDE in O$_2$-saturated 0.1M KOH solution at different rotation speed. The experiments were performed with a scan rate of 10 mV/s vs RHE. The RDE voltammograms shows the promising ORR activity of the synthesized catalyst. These doped graphene catalyst will be used in a PEFC to analyse its performance in a real fuel cell environment.

![ORR performance of the synthesized N-doped Graphene catalyst in 0.1M KOH](image)

**Figure 5:** ORR performance of the synthesized N-doped Graphene catalyst in 0.1M KOH

4. Conclusion

It has been observed that nitrogen doping of the biomass derived graphene can be achieved without adding any doping agent during pyrolysis. It has been confirmed with the help of a CHN analyzer (Make: Perkin Elmer; Model: 2400 CHNS/O Series II System) that the raw biomass itself has a nitrogen content of 8.2188 At%. This nitrogen content acts as a doping agent during pyrolysis. XRD analysis shows that the in-situ Nitrogen present in the lattice of parent material creates defects seen as broad peaks at 2θ=24.5° and 43°. Raman spectra analysis shows presence of D-band, G-band and D’ band corresponding to peaks at 1376 cm$^{-1}$, 1607 cm$^{-1}$ and 1650 cm$^{-1}$ respectively. The I_D/I_G ratio of synthesized NG has been found to be is approximately 0.86. The presence of in-situ nitrogen is confirmed through EDS study, where nitrogen shows a composition of 21.55%. Visual analysis through TEM shows presence of multilayer or stacked graphene. X-ray photoelectron spectroscopy shows the presence of pyridinic and graphitic nitrogen in the pyrolyzed cocoon and thus has a high catalytic activity. The RDE analyses of the synthesized NG revealed the catalytic activity of the catalyst towards ORR. The synthesized nitrogen doped graphene has the potential to be a low cost catalyst of high activity.

Acknowledgement

The authors would like to acknowledge the financial supports given for this work by the Science and Engineering Research Board, Government of India, (ECR/2015/000308) and University Grants Commission, Government of India, [F.30-315/2016(BSR)]. The corresponding author also acknowledge the International Travel Support (ITS/2018/005330) granted by Science and Engineering Research Board, Government of India, to present this paper in International Conference on Sustainable Energy and Green Technology 2018, 11th to 14th December 2018, in Kuala Lumpur, Malaysia.

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