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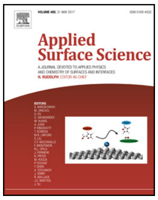

Full Length Article

One pot solvothermal synthesis of ZnPc nanotube and its composite with RGO: A high performance ORR catalyst in alkaline medium

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ABSTRACT

In recent years, sustainable energy resources in green environment are being extensively investigated. In pursuit of an efficient electrocatalyst for oxygen reduction reaction (ORR) in fuel cells, though pure platinum (Pt) is the unchallenged workhorse but high price, limited reserves and other factors has triggered the researcher to look for non Pt alternatives as catalysts. Metal based Phthalocyanine is one such prospective electrocatalyst for ORR in fuel cell. Herein, our work demonstrates the synthesis and ORR performances of Zinc Phthalocyanine (ZnPc) nanostructure and its composites with reduced graphene oxide (RGO). Electrochemical measurements show that the composite material exhibits better performances than pristine nanostructure in terms of limiting current density, onset potential, and half wave potential in alkaline medium. The improved electrochemical activity is attributed to the π–π interaction between ZnPc and RGO and also to the novel properties of graphene. The fascinating performances of ZnPc/graphene makes it a new viable electrocatalyst for different energy materials.

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1. Introduction

The research and progress of energy conversion and storage devices based on renewable sources are in great demand owing to its high energy density and low carbon footprint. Oxygen electrocatalysis becomes the building block of renewable energy technologies, based on three oxygen electrode reactions in basic electrochemical cell viz, Oxygen reduction reaction (ORR), Hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Oxygen electrochemistry based applications such as metal–air batteries, fuel cells, fuel synthesis, electrocatalytic and photocatalytic water splitting etc. are gaining increasing demand in industry.

Low temperature fuel cells, an energy conversion device that convert chemical energy to electricity, are being extensively used in various applications including transportation, stationary and potable power generation etc. The electrodes in these devices are basically made from platinum (Pt) group metals which belong to the family of critical raw materials catalyst. But the scarcity and high price of Pt group metal led the practitioners to search an alternative catalysts material for large scale industrial application in fuel cell technology. Replacement of most efficient commercially available Pt- based electrocatalysts is highly challenging till now, from the point of view of practical application in ORR.

ORR is a crucial cathodic reaction in Direct Methanol Fuel cells (DMFC) which operates by the oxidization of methanol to CO_2 and reduction of O_2 to water. But crossover of methanol from anode to cathode through electrolyte becomes very common phenomenon using Pt based electrocatalysts which, in turn, reduces the efficiency of DMFC [1]. Therefore, engineering other highly durable electrocatalysts is most desirable for DMFC for practical application. However,the reduction of O_2 follows multi-electron reaction with two possible pathways. In alkaline medium ORR mechanism can be achieved by the following reactions

$$O_2 + H_2O + 2e^- \rightarrow HO_2{}^- + OH^- \quad \text{(for 2-electron pathway)}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{(for 4-electron pathway)}$$

As two electron pathway produces H_2O_2 which is potentially hazardous, it is desirable to reduce O_2 to water via four electron pathway to achieve maximum energy capacity. ORR reaction occurs rapidly in alkaline medium than acidic medium. Also alka-

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line medium gives less corrosive environment to electrochemical cell which is a desirable criterion in fuel cell.

In search of suitable electrocatalysts, Metallophthalocyanines (MPc) is under focus due to their unique properties in versatile fields [2–5]. The macrocyclic nature of MPc with extended π–system accelerates the redox process which makes the material a suitable component in photochemical and electrochemical processes [6]. In 1964, Jasinski first used a N_4-chelate complex with a transition metal to reduce oxygen electrochemically in fuel cell [7]. But MPcs suffer from severe degradation by ORR intermediates which limits it practical application in fuel cell. On the other hand, surface supported/nanoparticle decorated MPcs lead to the enhancement of properties due to the coupling with surface which influences the construction of the hybrid material to promote the performances in versatile applications [8–16]. Carbon supported materials such as carbon powder, carbon nanotubes [17–19], graphene and heteroatom doped graphene [20–22], carbon nanotubes/graphene composites, mesoporous carbon can greatly enhance the ORR performances due to their large surface area, high electrical conductivity and have chemically active defect sites [23–27]. Significantly, graphene or graphene oxide can serve as support matrix for active MPc owing to its covalent interaction and π-π interaction with the giant 2D π–system which promote the performance. Furthermore, being attached on graphene support the solubility of MPc has been improved. Also slow electron transfer kinetics arising from MPc has been significantly enhanced as the graphene support provides supplementary active sites for ORR [28]. For instance, Iron Phthalocyanine (FePc) attached on large graphene sheet showed superior electrochemical performances than pristine material. Besides, the properties of this hybrid material are comparable with commercial Pt/C catalyst in terms of stability, methanol tolerance, anti-CO poisoning effects and ORR performances in alkaline medium [29]. Chen et al. used a carbon supported CoPc and FePc composite materials as catalysts and found more positive onset potential for FePc/C than CoPc/C in 0.1 M NaOH solution [30]. Li and his coworker showed good electrocatalytic activity of ORR for MWCNT supported CoPc macrocyle in 0.5 M H_2SO_4 [31]. Wang and his group carried out extensive study on multielectron transfer in ORR and in photocatalysis mechanism using different types of catalysts as well as graphene based catalysts [32]. Mao et al. reported for the first time 3D crumpled graphene (CG)–cobalt oxide nanohybrids as a high-performance bi-functional electrocatalyst in 1 M KOH. The nanohybrids showed excellent durability and high positive onset potential compared to that of commercial Pt/C in alkaline solution [33]. Sonkar et al. have synthesized MWCNT decorated with Cobalt Porphyrin and studied its application towards ORR in acidic, basic, and neutral medium which showed 4–electron reduction process with satisfactory operational stability and sufficient methanol tolerance ability [34].

As the central metal atom in Phthalocyanine is pivotal to determine the catalytic activity of the system, FePc and CoPc are considered to be ideal candidate for the redox active central metal atom [35]. To our knowledge there is no report on electrochemical activity of ZnPc. Also the electrocatalysis based on unsubstituted Phthalocyanine nanostructure is scarce in the literature. Herein, we report a facile solvothermal route to synthesize Zinc Phthalocyanine (ZnPc) nanostructure and it's composite with reduced graphene oxide (RGO) via simple *in–situ* reduction in solution using hydrazine hydrate. To the best of our knowledge, no one has reported earlier about the solvothermal synthesis of unsubstituted ZnPc using Zinc Acetate as precursor material and its use as electrocatalyst. Electrochemical measurements of pristine material as well as composite material demonstrate superior catalytic activity of composite, which is attributed to the synergistic effect between ZnPc and RGO. The methanol tolerence of composite material was also examined and found to be better than Pt/C. For ZnPc and RGO/ZnPc composite materials, the ORR performances and comparison with those of Pt/C are documented in this work. This graphene supported ZnPc nanostructure can be used as Pt free electrocatalyst in metal–air batteries and methanol fuel cell applications. The investigation is still carrying on for the further development of more active electrocatalyst based on RGO/ZnPc by changing the ratio of the component material.

2. Experimental

2.1. Materials and reagents

Phthalonitrile ($C_6H_4(CN)_2$)was purchased from Merck, Germany. Zinc Acetate dihydrate ($Zn(CH_3COO)_2$ $2H_2O$), ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}$ $4H_2O$), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), ethanol, sulfuric acid (H_2SO_4), hydrochloric acid (HCl), ethylene glycol and N,N, dimethyl formamide (DMF) were purchased from Merck, India. Graphite powder was obtained from Alfa aesar. All reagents were used without any further purification.

2.2. Synthesis

Graphene Oxide (GO) was synthesized by modified Hummers' method [36]. Briefly, a small amount of flake graphite along with $NaNO_3$and $KMnO_4$ in concentrated H_2SO_4 has been vigorously stirred, keeping the beaker on an ice bath. After that, water was carefully added to maintain the temperature at 90 °C followed by the addition of 30 wt.% aqueous solution of H_2O_2 in order to complete the oxidation. Inorganic anions and other impurities have been removed through repeated washing by 3 wt.% aqueous solution of HCl and DI until the pH becomes 7. The desired GO dispersion was then start to collect and finally it was dried in oven at 70 °C to obtain loose brown powder. On the other hand Zinc Phthalocyanine (ZnPc) nanostructure has been synthesized in one pot solvothermal method described below. In a typical synthesis, 0.45 mmol of Zinc Acetate with 1.8 mmol of Phthalonitrile and 10 mg ammonium heptamolybdate were mixed in 12 ml ethylene glycol in a teflon lined autoclave and kept it at 180 °C in a preheated oven for 24 h. After cooling down naturally to room temperature the precipitate was filtered and washed with HCl, ethanol and water repeatedly until the deep purple colour precipitate of ZnPc was found. The material was then dried in oven at 60 °C for overnight. Now equal amount of GO and ZnPc were mixed in DMF solution followed by the addition of hydrazine hydrate and ammonia solution at 90 °C. After 2 h, the resultant material was collected via centrifugation and washed in DI for 3 times. The material thus obtained, after drying for 6 h, was re-dispersed in DMF and used for characterization and other desired applications.

2.3. Characterizations

The phase purity and crystal structure of the as synthesized material was characterized by X-Ray diffraction (XRD, D8 Advance ECO,Cu-Kα radiation ($\lambda = 1.54$ Å)). The chemical structures of ZnPc and RGO/ZnPc nanocomposites were analysed by Fourier transform infrared (FTIR) spectroscopy (Shimadzu IRPrestige-21, spectral resolution $0.5\,cm^{-1}$) and Raman spectroscopy by confocal raman spectrometer (alpha 300, Witec, Germany, Laser Source of wavelength 532 nm). Morphologies of ZnPc nanostructure and RGO/ZnPc nanocomposites were characterized by Field emission scanning electron microscope (FESEM, Hitachi S-4800). The absorbance spectra of the ZnPc and RGO/ZnPc were measured using a UV-VIS-NIR Spectrophotometer (UV3600, Shimadzu). For UV–vis measure-

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