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Energy

Electrocatalytic hydrogen evolution reaction on nano-nickel decorated graphene electrode

Nilesh K. Mahale[*], Sopan T. Ingle

School of Environmental and Earth Sciences, North Maharashtra University, Post Box # 80, UMAVI Nagar, 425001 Jalgaon, MS, India

A B S T R A C T

The quest for the replacement of noble metal electrocatalyst for the hydrogen evolution reaction (HER) with lowest overpotential and Tafel slope is still a major challenge. In the present work new concept of earth abundant material like transition metals (Ni) are composed with graphene sheets as a catalyst to increase the rate of hydrogen production. The nickel nanoparticles are decorated uniformly on graphene sheets via electrophoretic deposition (EPD) method to enhance it's HER performance in alkaline solution. The composite is characterized by XRD, FTIR, XPS, SEM and TEM techniques. The composite shown improved HER performance with a low overpotential of 65 mV for 10 mA cm^{-2}, a small Tafel slope of 54 mV dec^{-1} and longtime stability.

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1. Introduction

Right from the human evolution and the industrial revolution, the human life is heavily depending on the fossil fuels for energy. Excessive utilization of fossil fuels is resulting in a gradual decrease in fossil fuel reserves along with environmental pollution; this is an alarming-call for the development of pollution free and sustainable energy sources. Hydrogen is abundantly present in the universe and it is a promising chemical fuel for the future due to its clean and renewable nature. Being an ideal clean energy carrier for the future, it has the highest energy density per unit mass and can be extracted from natural resources such as water [1].

Water electrolysis is conventional method of pure hydrogen and oxygen production, currently the electricity obtained from renewable sources to produce hydrogen is called green hydrogen and this makes hydrogen economically and environmentally appealing alternative as an energy sources [1–6]. Hydrogen production by electrolysis consumes high energy and this is also one of the reasons for ranking behind fossil fuel as an energy source in large-scale commercial applications. In order to produce hydrogen with minimum energy consumption, efforts are going to the creation of molecular system with the help of earth abundant elements and to achieve high efficiency, highly active and low over-potential electrode for hydrogen production, but still it remains a great challenge [7]. In the nature the noble metals are excellent electrode materials with high efficiency, high activity and having low over-potential despite of these properties their commercial applications are hindered by the high cost and low abundance [8,9]. Hence, the research for alternative to the noble metals is the need of hour, in the quest of such material the nano composites beacon with its potential properties to be a reasonable alternative. The 3d transition metals are having potential applications, especially Ni is one of the metals which having distinctive properties and potential applications in many fields, like lithium ion batteries, magnetic materials and catalysis [10–12]. In the d block elements, especially the transition metal like Ni is considered as a good contestant for HER due to its high electrocatalytic activity and low cost [13,14].

The excellent resistance to corrosion, superior thermal stability and mechanical strength these properties are found in carbon nanomaterials eg. graphene, carbon nanotubes and carbon nanofibers and these have been widely exploited as a catalyst substrate in HER. Electrophoretic deposition (EPD) method is an efficient and adaptable method to grow nano-metal on graphene surface (nanocomposite) with large specific area, high electrocatalytic activity and superior mechanical properties. The reduction of graphene oxide typically been done by chemical agents such as hydrazine or strong alkaline solutions, but the EPD is a low cost and

* Corresponding author.
E-mail addresses: nileshmahale@gmail.com (N.K. Mahale), sopan.ingle@gmail.com (S.T. Ingle).

environmentally friendly process [15–17]. The EPD method has a number of advantages in the preparation of high deposition rate, good thickness controllability, good uniformity, and simplicity of scale up. In this work we decorated Nickel nano particles on graphene by EPD. The composite obtained by this method used as a non-noble-metal hydrogen evolution reaction catalyst, nanocomposite maintained its activity under alkaline conditions with a Faradaic efficiency of ~100%. The lowest onset overpotential ~10 mV and an overpotential (η) of ~65 mV at current density of 10 mA cm^{-2} is maintained.

2. Experimental section

2.1. Preparation of graphite oxide

Graphite oxide was prepared by modified Hummer's method, by stirring 100 mg graphite powder and 50 mg sodium nitrate in 3 ml sulphuric acid. The above suspension was kept in a round bottom flask (RBF) under ice bath with vigorous agitation, and RBF was kept under ice bath with the addition of potassium permanganate ($KMnO_4$) over 30 min. The rate of addition of $KMnO_4$ was maintained enough to control the temperature of suspension from exceeding 20 °C. After 30 min ice bath was removed and the temperature was allowed to rise up to 35 °C for 2 h and as the reaction progressed the mixture became a brownish gray paste. At the end of 2 h, 100 ml distilled water was added drop by drop for 15 min and the temperature of the reaction was maintained at 90–95 °C. After distilled water addition, the suspension turned brown in color, and then 100 ml 30% hydrogen peroxide (H_2O_2) was added to minimize the concentration of residual permanganate and manganese dioxide to colorless soluble manganese sulfate. After treatment with H_2O_2, the suspension turned in bright yellow color.

For collection of the graphite oxide paste, it was centrifuged at 9000 RPM for 15–20 min. The supernatant from centrifuged was discarded and collected the graphite oxide. The graphite oxide paste was washed by 10% hydrochloric acid and subsequently with distilled water till it becomes neutral (pH 7); mother liquor was tested by atomic absorption spectrophotometer (Thermo) to ensure the filtrate is completely manganese free and then transformed it into powder form by evaporating the water.

2.2. Exfoliation of graphene oxide by sonication

For exfoliation of graphene oxide, 400 mg graphite oxide was sonicated in 400 ml N-methyl-2-pyrrolidone (NMP) for 2 h. In order to remove large particles the suspension was centrifuged at 5000 rpm for 30 min. The supernatant of the above suspension was decanted and filtered through a poly-tetrafluoroethylene (PTFE) membrane before dispersing the obtained filtered cake of exfoliated graphene Oxide in ethanol. After dispersing the exfoliated graphene oxide cake in ethanol; it is again sonicated for 10 min and filtered. The dispersion and filtration are repeated four to five times to make the graphene oxide cake NMP free. After final filtration this cake was redispersed in ethanol and centrifuged at 5000 rpm for 30 min, the supernatant was decanted and further sonicated for 1 h to get the homogeneous graphene oxide dispersion in ethanol [18].

2.3. Synthesis of nano-nickel decorated graphene oxide composite

Individual nickel nanoparticles were synthesized on graphene oxide surface by simultaneous sonication and reduction of nickel salt solution and exfoliated graphene oxide, using hydrazine hydrate ($N_2H_4 \cdot H_2O$) in the presence of sodium hydroxide. The use of hydrazine hydrate in aerobic condition leads to the formation of nickel oxide nanoparticles by chelation; Ni nanoparticles formation

takes place through reduction of Ni^{+2} by $N_2H_4 \cdot H_2O$. This method is more facile than conventional. Composite was prepared of Ni:Graphene oxide, in the ratio i.e. 2:8. Keeping in mind the molar ratio of Ni:N_2H_4:NaOH, the Ni salt solution (16.8 mM) was prepared by dissolving 400 mg $NiCl_2 \cdot 6H_2O$ in 100 ml water, Sodium hydroxide 15 mg in 100 ml water, in this sodium hydroxide solution 400 mg exfoliated graphene oxide was dispersed and mild sonication was done to get homogeneous dispersion of exfoliated graphene oxide. 5 ml hydrazine hydrate was taken in Erlenmeyer conical flask of 250 ml capacity and kept in sonication bath (750 W, 50 kHz, Ultrasonic cleaner, Lab Hosp, Mumbai) when the temperature of water in sonicator reached 45–50 °C, drop by drop addition of exfoliated graphene oxide suspended sodium hydroxide and nickel chloride solutions were started simultaneously and sonicated throughout the experiment. First the bis- and tris-nickel hydrazine chloride complex of purple and blue color are formed at 60–70 °C; within 5–10 s solution turns black and it represents the formation of metal nickel nanoparticles. Being sonicated the aggregation of nickel particles was avoided. After finishing the reaction, composite was collected by centrifugation at 9000 rpm, cake was washed several times to make it free of base and non-reacted material. All reagents used in the experiment were of analytical grade provided by Fisher Scientific Company and the water used throughout the experiments was ultrapure and produced by a Milli-Q SP Ultrapure-Water Purification system [19].

2.4. Electrophoretic deposition of Ni-Graphene

A single compartment electrophoretic deposition cell was setup; Ni-Graphene composite was dispersed in Milli-Q water and sonicated for 2 h at 30–35 °C for uniform and stable suspension in water containing 1 mg/ml nickel-graphene oxide composite. A copper foil of $25 \times 70 \times 0.1$ mm in size was used as the working positive electrode, and a stainless steel plate as the negative electrode. Before the electrophoretic deposition, the copper working electrode was polished by grit silicon carbide paper (220–300, 1000–1600 grit), and then the foil was dipped in acetone for 10 s, in Milli-Q water for 10 min, in acetic acid for 10 min, again with water for 10 s, then sonicated in acetone for 5 min and finally rinsed with iso-propyl alcohol. One side of the copper foil was covered by a Teflon adhesive tape to expose known area. The electrodes were vertically oriented and separated by 1 cm in a beaker containing Ni-Graphene oxide composite suspension. A direct-current voltage of 10 V was applied (Dot-tech 4124 DC power supply) for 30 min. After deposition, the sample was air-dried at room temperature for 24 h [20].

2.5. Physical and electrochemical characterization

The morphology of the electrophoretically deposited nano-nickel-graphene composite was characterized using Hitachi High Tech S-4800 Type II equipped with EDX Brucker-X Flash Detector 5030. The X-ray diffraction (XRD) patterns were obtained using the Brucker D8 Advance powder diffractometer operating in the reflection mode with CuKa radiation (40 kV, 40 mA) and diffracted beam monochromator, using a step scan mode with a step of 0.020 and 0.5 s per step, divergence slit 1.200 and antiscatter slit 0.600 were used. The Transmission Electron Microscopy (TEM) was done by Philips CM200 TEM, having an operating voltage range of 20–200 kv with resolution: 2.4 Å. Ion milling method was used for sample preparation in TEM analysis, this was a single beam machine in which copper substrate of the sample was thinned by ion milling. The sample was placed in the cathodic side, and thinned upto thickness of 120 nm [21]. Chemical state and reduction degree of reduced graphite oxide were analyzed using X-ray photoelectron