

Synthesis of Graphene Supported Nickel and Cobalt Nanoparticles and Their Applications for Methanol Oxidation in Alkaline Medium

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Abstract—In various applications fuel cells are considered very attractive devices to obtain clean electrical energy directly from the combustion of chemical fuel. During the last decade much attention is given to the direct methanol fuel cells (DMFCs) because methanol is inexpensive, easily available and transported liquid fuel. Mostly platinum is employed for the electro-oxidation of methanol as an anodic material however higher economic costs and poor oxidation kinetics are the main problems of platinum based catalyst. In this paper we reported the synthesis of graphene oxide (GO) by modified Hummer's method and synthesis of graphene supported cobalt and nickel nanoparticles by simple chemical solution synthesis method. The synthesized materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and EDX. The electrocatalytic properties of the synthesized catalyst for methanol oxidation were investigated by cyclic voltammetry.

Keywords— Graphene, Graphene oxide, Direct methanol fuel cells, Nanocomposites, Electrocatalysts, Methanol oxidation.

I. INTRODUCTION

Under the global sustainability prospective, sustainable development involves four key factors in terms of social, environmental, economic and energy resources sustainability. Therefore energy derives the global economy and is considered as key element for the climate and the sustainable development. Sustainable development requires sustainable supply of clean and cheap sources of energy that do not have adverse social and environmental impacts[1][2]. Globally, about 87% of total energy is produced by fossil fuels and only 6% is generated in nuclear power plants and only 7% comes from renewable resources (hydro, wind, solar, geothermal and biofuel). Unfortunately, this planet has limited amount of fossil and nuclear energy resource and at the same time generation of energy can contribute to degradation of local environment such as global warming, acid rain and ozone layer depletion ultimately the climate change[3]. In order to overcome all these critical challenges of energy security and environmental degradation attempts have been made in the development

of advance, affordable and environment friendly energy harnessing technologies.

In this regard innovative energy technologies has got considerable attention during the last few decades. Among them fuel cell is considered as promising power generation technology both for mobile and stationary applications[4].

Success of DMFC to be competitive as viable energy source in the energy market depends upon the cost, efficiency and durability of the electrocatalyst. At present, most of the fuel cells (low temperature fuel cell) use Pt-based catalyst. Due to these expensive electrocatalyst manufacturing cost of the fuel cell is increased which greatly affects the successful commercialization[5]. Beside these most of the Pt-based electrocatalyst face catalyst poisoning. Consequently researchers are trying to develop a low cost, reliable and efficient electrocatalyst to replace Pt-base catalyst[6].

So far significant numbers of studies have been performed by involving different techniques for the electro-oxidation of lower molecular weight organic compounds such as CH_3OH , HCOOH , and HCHO . Results from these investigations reveals that at low temperature electro-oxidation of these organic compounds need the presence of Pt-based catalyst[7]. Two key steps dehydrogenation and chemisorption of CO are involved during the electro-oxidation of these compounds under Pt-based catalyst. A strongly adsorbed intermediate species (like CO, CHO) are produced during all these reactions. These types of species like CO, CHO are adsorbed on the surface of the catalyst and cause for catalyst poisoning[8]. The poisoning effect of the Pt catalyst significantly decreases power density and fuel consumption efficiency of the cell. To inhibit the poisoning effect and to increase the electro-oxidation rate by an order of three to four times a lot of research have been carried out to replace the Pt catalyst[9]. Most suitable results have been achieved by alloying the Pt with Ru and Sn for the complete oxidation of methanol and CO into CO_2 [10]. In recent years research is focused to develop non noble metal electrocatalysts such as Co, Ni, Pb, and W to replace platinum an expensive metal. However above transition metals show poor oxidation kinetics. By using high conductive material as a support like graphene, carbon nanotubes (CNTs) and carbon nanofibers,

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electrocatalytic efficiency of these metals can be improved. Compared with other carbon support material graphene is an excellent electrode material because of its lower manufacturing cost, high surface area, and exceptional conductivity[11]. Therefore, graphene can be used as a catalytic support material to enhance the electrochemical activity of catalyst particles for methanol and ethanol oxidation[12]. In our present work we synthesized Ni/graphene and Co/graphene nanocomposites by a facile, economic and environmental friendly method. Furthermore, the synthesized materials were characterized by XRD, SEM and EDX. The electrochemical activity of the synthesized electrocatalyst towards methanol oxidation was characterized by cyclic voltammetry technique.

II. EXPERIMENTAL

A. Material and Reagents

Graphite Powder (99.99%) of particle size 45 μm , H_2SO_4 (98%), NaNO_3 (99%), KMnO_4 (99%), H_2O_2 (30%), $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Ethylene Glycol, NH_3 were purchased from Sigma Aldrich (USA). All the reagents were of analytical grades and used without further purification.

B. Preparation of Graphene Oxide (GO)

Graphene oxide (GO) was synthesized from graphite powder by modified Hummer's method[13]. In the typical procedure 1g of graphite powder(99.99%) was obtained and mixed with 25ml 98 % sulphuric acid (H_2SO_4), and 1g of sodium nitrate (NaNO_3) taken in an ice bath for three hours followed by the gradual addition of 5g of KMnO_4 . The reaction was kept under vigorous stirring at 30 $^\circ\text{C}$. Then slow addition of 100ml water is performed. After this the obtained product was placed at 85 $^\circ\text{C}$ for two hours, then reaction was treated with 10ml hydrogen peroxide (H_2O_2 30 %). Finally, the obtained yellowish cake was centrifuged in order to get pure product where solution was washed several times with distilled water and ethanol.

C. Preparation of Ni/Co Graphene Nano composites

In the present work deposition of nickel nanoparticles on graphene was obtained by using simple solution synthesis method[14]. In this method we used ethylene glycol as a solvent and hydrazine hydrate as a reducing agent. In the typical procedure, 262.8mg of nickel sulfate hexa-hydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), and 100mg of graphene oxide that was obtained from graphite powder oxidation by a modified Hummer's method. Nickel salt as metal precursor and graphene oxide were added in a 100ml flask having 60ml ethylene glycol that was used as a solvent. After that the mixture was ultrasonicated for an hour, then stirring was performed for 24 hours at ambient temperature. Then ammonia solution was added into the solution while constant stirring in order to gradually decrease the pH of the solution to 10.5. After that 1.0ml hydrazine hydrate was added as a reducing agent into the above solution and the reduction reaction was performed under constant stirring at 85 $^\circ\text{C}$ for 12 hours. The obtained product was then filtered in order to get

pure product, washing was performed various times with distilled water and ethanol and dried in a vacuum desiccator at room temperature. Same procedure is adopted for the synthesis Co/graphene nanocomposites.

D. SEM /XRD Characterization

In order to investigate the phase, crystal structure and lattice parameter of the prepared nanocomposites, X-ray powder diffractometer (STOE Germany) with computer interface was used having radiation source Cu K α at $\lambda = 1.5418 \text{ \AA}$. The scan angle 2θ was selected 0 $^\circ$ -80 $^\circ$ with step size 0.04/sec.

To study the surface morphology of the synthesized catalyst Scanning Electron Microscope (HITACHI SU- 1500) with 50 μm magnification was used and voltage was kept up-to 15 kV.

E. Electrochemical Measurements

All the electrochemical measurements were performed by using AUTOLAB 4.9 Potentiostat connected to PC. We used Ag/AgCl electrode as reference electrode in this work. The counter electrode was a Pt wire 1mm thick and 12cm long. 1M KOH solution was used as a supporting electrolyte with 3M methanol concentration in a conventional three-electrode Pyrex glass electrochemical cell. The electrochemical characterization of the prepared Ni/graphene and Co/graphene nano-composites was done by using cyclic voltammetry technique. In the present work, glassy carbon electrode with active area 0.071 cm^2 was modified as working electrode. The working electrode was first washed and cleaned with distilled water than polished with alumina slurry. For the modification of working electrode a homogenous slurry of the functional material was prepared by mixing 2 mg fine powder of the active material, 20 μl of nafion solution and 400 μl of isopropanol. After sonicating the slurry for 30 min at room temperature, 15 μl from the prepared slurry was poured on the active surface of the glassy carbon electrode which was then air dried at room temperature. The obtained current densities were normalized based on the utilized surface area of the modified glassy carbon electrode. The response of peak current was checked at various scan rates ranging from 25mVs $^{-1}$ to 100mVs $^{-1}$ at starting potential starting from 0 mV to 1800 mV positive vertex potential.

III. RESULT AND DISCUSSION

To investigate the successful synthesis of nano-composites characterization was done by performing X- ray diffraction and scanning electron microscopy. XRD pattern of graphene oxide (GO) is shown in the figure 1(a). The characteristic peak is obtained at 2θ of 11.5 $^\circ$ clearly indicates the synthesis of graphene oxide, which shows that effective oxidation of graphite leads to the formation of graphene oxide. The XRD pattern of prepared Co/graphene nanocomposites is shown in the Fig.1. (b) The typical reflection peak at $2\theta = 22.3^\circ$ indicates the formation of graphene by the reduction process of graphene oxide. On the other hand, the diffraction bands obtained at $2\theta = 37.4^\circ$, 44.3 $^\circ$ and 63.2 $^\circ$, 76.1 $^\circ$ can be assigned to the characteristic of face center cubic (fcc) structure of Co

nanoparticles.

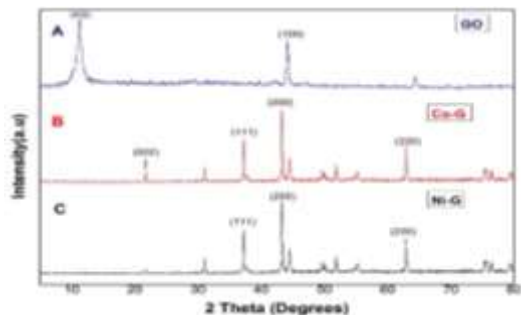


Fig 1. (a) XRD pattern of graphene oxide (b) Co/graphene (c) Ni/graphene

The XRD display of Ni/graphene nanocomposites is shown in the Fig.1c. The typical reflection peak at $2\theta = 22.3^\circ$ indicates the formation of graphene which was obtained by the reduction process of graphene oxide. On the other hand, the diffraction bands obtained at $2\theta = 37.4^\circ, 44.3^\circ$ and $63.2^\circ, 76.01^\circ$ can be assigned to the characteristic of face center cubic (fcc) structure of Ni nanoparticles. Cobalt and Nickel have almost similar crystal structure under normal conditions due to closer atomic numbers and molecular weights. That is the reason XRD patterns of Ni and Co are almost similar.

The morphologies of the synthesized materials were characterized by scanning electron microscopy (SEM). Figure.2 (a) represents the low magnification SEM image of graphene oxide from this image the morphology of the secondary particles can be clearly visualized. There might be the chance of agglomeration among the particles. Fig 2 (b) represents the high magnification SEM image of graphene oxide. From this image it can be seen that most of the graphite oxide has been successfully exfoliated to wavy type ultrathin structure of graphene oxide sheets.

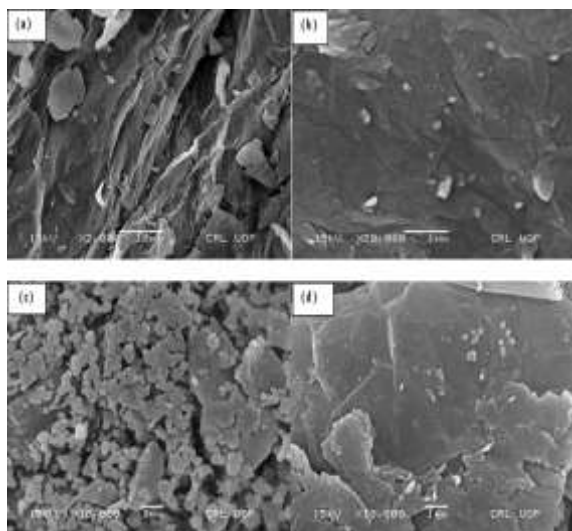


Fig2. SEM image of the (a) graphene sheets (b) Ni/graphene and (c) Co/graphene

Fig. 2c represents the SEM image of Ni/graphene nanocomposites which reveals that Ni nanoparticles are uniformly dispersed on graphene sheets. Fig. 2 d represents the randomly dispersed Co nanoparticles on graphene sheets

Figure 3 shows the EDX analysis of Ni/graphene and Co/graphene nanocomposites catalysts. The EDX analysis in the fig 3a shows that

Co/ graphene nanocomposites catalysts was composed of C, O and Co elements. Figure 4 b represents the EDX spectrum of Ni/ graphene catalysts which reveals that Ni/graphene nanocomposites catalysts was composed of C, O and Ni elements.

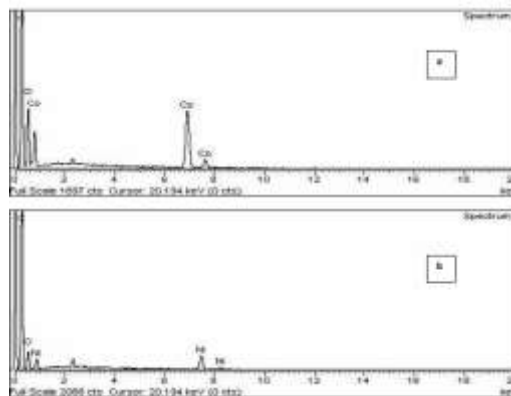


Fig 3. EDX analysis of (a) Co/graphene (b) Ni/ graphene

The presence of carbon peaks in both the samples represents the formation of graphene sheets and small oxygen peak reveals that graphene also contains small quantity of carboxyl and hydroxyl groups.

3.1 Cyclic Voltammetry

In order to investigate electrochemical behavior of prepared Ni/ graphene and Co/graphene cyclic voltammogram was recorded on modified glassy carbon electrode as a working electrode. The cyclic voltammogram (CVs) of Ni/graphene and Co/graphene nano-composites for methanol oxidation was done in alkaline medium. For the comparison cyclic voltammogram of bare GCE, Ni/ graphene and Co/graphene were recorded under same conditions at a scan rate of 100 mVs⁻¹, 1M KOH and 3M methanol concentration.

Interestingly it can be seen in the Figure.4 Co/graphene modified electrode showed higher current density during forward scan as compared to bare GCE and Ni/ Graphene electrode.

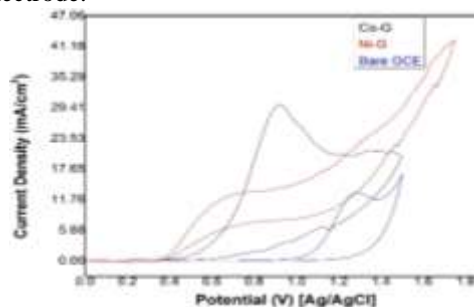


Fig 4. Cyclic voltammogram of bare GCE, graphene supported Ni and Co nanoparticles at a scan rate of 100 mVs⁻¹ at ambient temperature

The anodic peak current observed for the period of forward scan was due to the electro-oxidation of methanol into intermediate species and further complete oxidation of these species into CO₂, H₂O and electrons. During the reverse scan, oxidation peak is obtained due to the remaining species that was not fully oxidized during the forward scan. The cyclic voltammogram of bare GCE electrode, Ni/graphene and Co/ graphene nanocomposites are shown in the fig. 04.

IV. CONCLUSION

Ni/graphene and Co/graphene nanocomposites have been synthesized by using chemical reduction method from metal salts and graphene oxide, which was already prepared by the oxidation of graphite powder by using modified Hummer's method. The electrocatalytic properties of these synthesized nanocomposites for methanol oxidation were tested in alkaline medium. It has been observed that Co/graphene nanocomposites showed higher electrochemical activity as compared to Ni/graphene. However, comparing the current densities of these nanocomposites is far less than Pt/graphene which is still unbeatable as electrocatalyst for methanol oxidation reaction. Electrochemical stability and potential towards oxygen reduction reaction of these nanocomposites still need further investigations.

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