Synthesis and Characterization Studies of Selenium Decorated Reduced Graphene Oxide Assisted Cobalt Acetate (Co $(AC_2)4H_2O$) Nanoparticles

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Abstract

The Oxygen Reduction Reaction (ORR) is the core technology for electrochemical reaction for Proton Exchange Membrane Fuel Cells (PEMFC). The precious metals electro catalysts are used as an active cathode catalyst due to their oxygen reduction reaction activity at low temperatures. Instead of Precious metals electro catalysts, the catalysts which is being prepared by non-precious materials is much needed. In this paper we easily and successfully synthesis selenium reduced graphene oxide and assisted cobalt acetate nano particles. The prepared samples are analyzed by X- Ray Diffraction analysis XRD, to confirm the presence of selenium, graphene and cobalt by the peaks, further the functional groups are studied by Fourier Transform Infrared analysis - FTIR. The morphology and the structure were identified by the Scanning Electron Microscope. The composition of selenium, graphene and cobalt are determined by the EDAX studies.

Keywords: Oxygen Reduction Reaction, graphene, cobalt, catalysts, fuel cells

I. INTRODUCTION

The problems of global warming, environmental pollution and energy risk were drawn greater attentions for the development of clean and sustainable energy sources [1]. The newly emerging field of nanotechnology has the potential to make a significant impact on the electro catalysts for the ORR by introducing novel nano scale materials [2]. The fuel cells have been receiving a lot of attention as a sustainable power source for transport, sustainable and portable applications because of their efficiency and low emission [3-6]. The Proton Exchange Membrane Fuel Cell (PEMFC) is considerable as an ideal power source for mobile and stationary applications [7]. The oxygen reduction reaction plays an important role in the overall performance of electrochemical energy devices, such as fuel cells and metal air batteries [8-11]. The exploration of non precious metal catalysts with high efficiency, low cost and superior durability to oxygen reduction reaction have been conducted as promising candidates to replace platinum based catalysts such as transition metals, nitrogen, carbon and etc. [12]. The transition metals shows catalytic behavior mainly due to the presence of vacant ‘d’ orbital and the ability to exhibit variable vacancies and the tendency to form complex compounds [13].TMOs have received considerable attention as anodic materials for use in batteries because of their superior theoretical capacity. Most of the transition metals are semiconductors thus their conductivity should be improved before applied to an electro catalyst [14]. Graphene, improves the conductivity, because it has a high surface area, good mechanical properties and high electrical conductivity, which help in improving the electrochemical properties of medal oxides [15]. Recently a large number of reports has been published on ORR electro catalysts, to reduce the cost of fuel cells electro catalysts, Two major approaches are currently very active i) To increase the platinum catalytic activity and reduce Pt content through alloying with other transition metal oxides such as Cr, Ni, Fe, Co and so on, ii) To improve the Pt utilization by increasing the surface area and dispersion of Pt nano particles using high surface carbon supports [16]. TMOs have received attention ex. HER [17], ORR [18], and solar cells due to their multifunction behavior and thus important as catalysts in PEMFC and ease of synthesis [19]. From these approaches we are prepared the materials by using the transition metal oxides. In the D block elements, The cobalt has greater ability in accepting atoms from other molecules and forming complex molecules needed in further chemical reactions, process and the cobalt can react to form more than one ion to exhibit catalysis thus allowing for a wider variety of reactions [20]. So we focus alloying the precious metal with another metal in order to increase the mass activity with respect to platinum and eliminating the need for platinum by producing non precious metal catalysts that can match platinum in catalytic activity.

II. EXPERIMENTAL SECTION

Preparation of Selenium Decorated Reduced Graphene Oxide (Se-rGO)

200 mg of graphite oxide was ultrasonically dispersed into 100 ml deionized water at 45^0C, then under stirring the 200mg of SeO_2 was added into the suspension of GO. The temperature maintained at 80^0 C for 2 hrs. Then the reducing agent hydrazine hydrate was dropped into the mixture. The resulting mixture was filtered by using whatmann filter paper and the prepared sample was washed well with deionized water and freeze drying. The product was labeled as Se-rGO.

Preparation of $CoSe_2$ Supported on Selenium Decorated Reduced Graphene Oxide ($CoSe_2$/Se - rGO).

0.023g of Na_2 SeO_3 is dissolved in 13 ml of Diethylene Triamine (DETA) solution to prepare solution A and 0.1350 g of Se-rGO and 0.0172 g of Co(AC)2. H2O is dispersed in 26 ml of water to prepare solution B. the two solutions were transferred to an autoclave, which was maintained at 180^{0}C for 16 hrs. Then the system was left cooled down to room temperature. The product was filtered by using whatmann filter paper and washed well with deionized water and freeze drying. The product was labeled as $CoSe_2$/Se-rGO.

III. RESULT AND DISCUSSION

X-Ray Diffraction Analysis

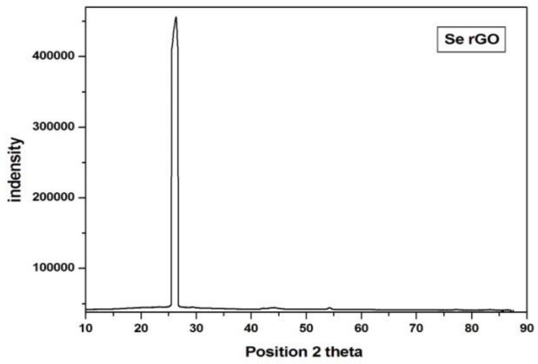

Fig:1 XRD spectrum of Se-rGo

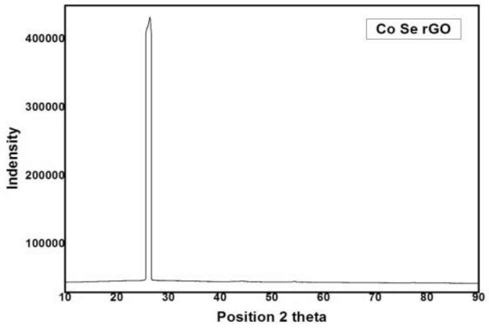

Fig:2 XRD spectrum of Co Se2/Se-rGo

The presence of phase structural transformation of the synthesized Se-r Go and Co Se_2/Se-rGo sample was characterized by X-Ray diffraction (Fig.1). X-Ray diffraction detection on a PAN analytical Xpert 3 with a Cu Kα radiation (λ=1.541Å). High intense peaks are noticed in the X-Ray diffraction pattern of the Se-r Go and Co Se_2/Se-rGo material, which confirm the nano crystalline nature of the material, the pattern does not contain any impurity peak, which confirm the purity of the material and phase. The broad diffraction beak Between 20^0 to 30^0 shows the presence of carbon. The crystalline size was calculated using the Debye Scherer's formula [21]. From the XRD results calculate the crystallite size of the materials was calculated using the relation.

$$\mathbf{D} = \frac{K\,\lambda}{\beta D\ \cos\Theta}$$

Here, **D** is the particle size, **K** is a constant (0.9) , **βD** is the peak width at half-maximum intensity, **λ** is the wave length, **Θ** is the peak position. The calculated crystalline size was 34nm. The peak position at 2Θ = 26.30, 29.44, 44.23 confirm the presence of Selenium and cobalt.

FTIR Spectrum Analysis

The FTIR spectra for all prepared samples are analysed using Bruker, Alpha T, model spectrometer and it ions recorded by KBr pellet technique from the range of 4000cm^{-1} to 4000 cm^{-1}. Fourier Transform spectroscopy is a technique which is used to obtain an infrared spectrum and to measure the vibrational frequencies of bonds in the molecule.

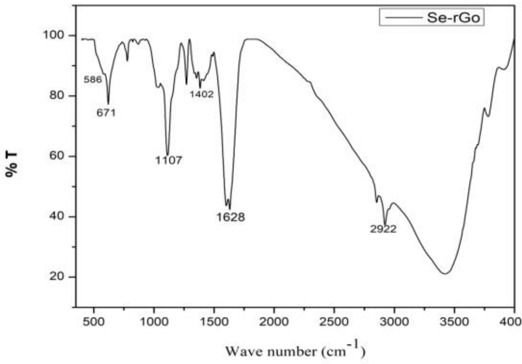

Fig. 3: FTIR spectra of prepared Se-rGo nano material

Fig 3 shows the FTIR spectra of prepared Se-rGo nano material, well defined absorption bands were observed at 586.61 cm^{-1} and 671 cm^{-1} [22] which is assigned at Co-O stretching vibration and O-Co-O bridging vibration. The wave length at 1107 cm^{-1} and 1402 cm^{-1} assigned at alkoxy group and carboxyl C-O [23]. The wave length at 1626 cm^{-1} assigned at unoxidized graphitic domains.

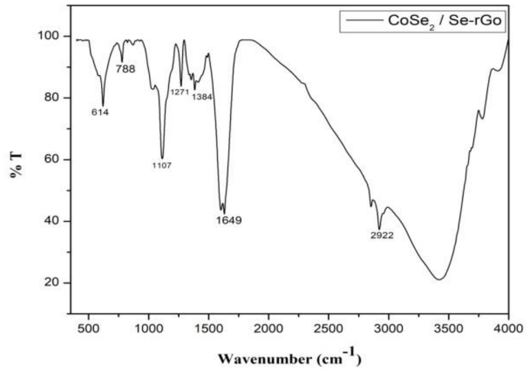

Fig. 4: FTIR spectra of prepared Co Se$_2$/Se-rGo nano material

Fig 4 shows that the FTIR spectra of Co Se$_2$/Se-rGo. The wavelength at 1052 cm^{-1} and 1251 cm^{-1} confirm the stretching vibration of C-O according to standard spectrum of cobalt acetate peak should be at frequency range 2980 cm^{-1} and 3526 cm^{-1}assigned the O-H bands [24]. 1649 cm^{-1} and the C-H bands near 2980 cm^{-1} are due to the presence of cobalt acetate residue [25].

SEM Analysis

Scanning electron microscopy is used for inspecting topographic of specimens at very high magnifications using a piece of equipment called the Scanning Electron Microscope. In order to obtain insight information about surface morphology and particle size of the samples, SEM analyses were performed. SEM analysis was carried out using Carl Zeiss EVO 18 at 25 Kx magnifications.

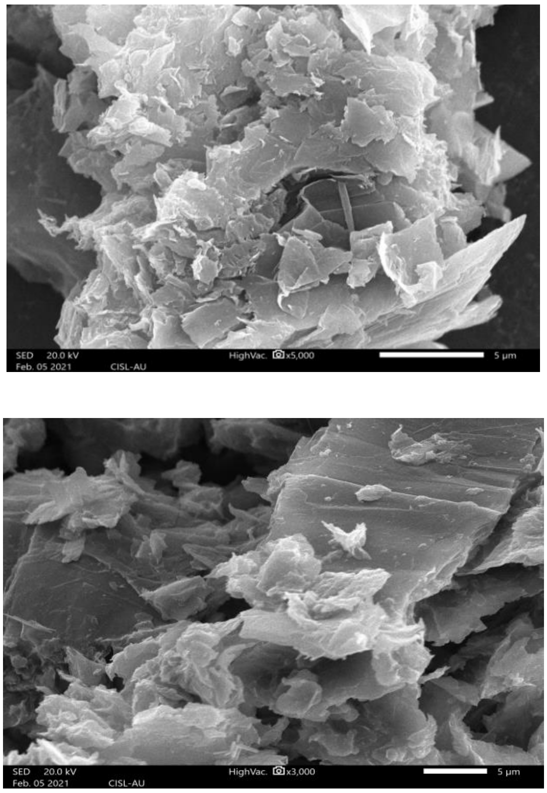

Fig. 5: SEM images of prepared Se-rGo nano material

Element	Line	Mass %	Atom%
Cu	K	4.96±0.22	6.09±0.27
Se	L	95.04±0.58	93.91±0.58
Total		100.00	100.00
Spc_001			

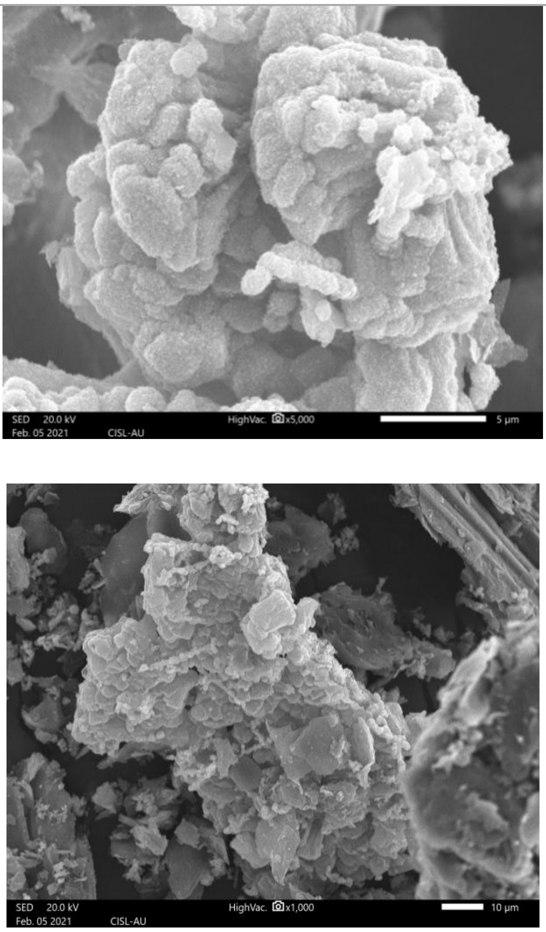

Fig. 6: SEM images of prepared Co Se2/Se-rGo nano material

The morphology of the synthesized Se-rGo and $CoSe_2$/Se-rGo nano materials examined by the SEM was shown in Fig 5&6. The images taken at various magnification size (10µm, 5 µm) the images shows the cabbage structure.

EDAX Analysis:

The Energy spectrum analysis technique was used to determine the composition of the sample. The EDAX spectrum of Se-rGo Fig (7) shows the presence of selenium, at 2KeV the presence of grapheme were present in the prepared sample. No appreciable quantities of Cu were observed over a number of surface sites.

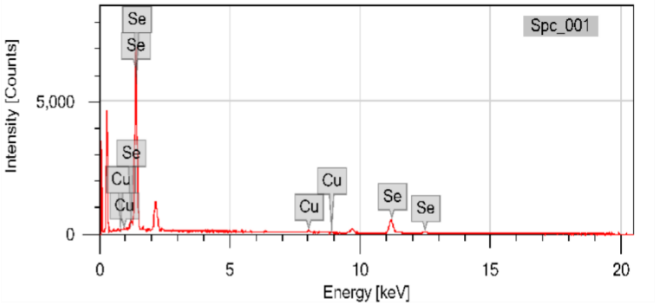

Fig. 7: The EDAX spectrum of Se-rGo

The EDAX spectrum of Co Se_2/Se-rGo Fig (8) shows the presence of cobalt and selenium, so we will confirm that the cobalt is assisted with selenium.

Element	Line	Mass%	Atom%
Co	K	28.59±0.67	34.92±0.82
Se	L	71.41±1.03	65.08±0.94
Total		100.00	100.00
Spc_001			

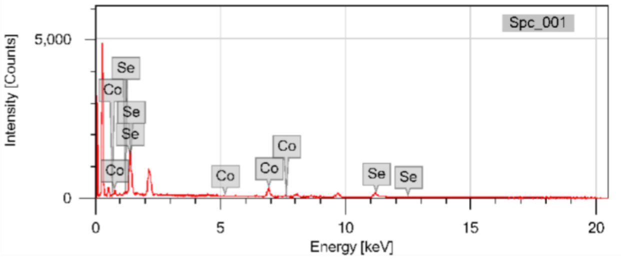

Fig. 8: The EDAX spectrum of Co Se2/Se-rGo

IV. CONCLUSION

Selenium decorated reduced grapheme oxide (Se-rGo) was successfully prepared and $CoSe_2$ was assisted into the Se-rGo, the phase structure and crystalline size were determined by the X Ray Diffraction analysis. The functional groups were presented in the prepared sample were identified using FTIR analysis. The morphology and composition of the prepared samples were analysed by Scanning Electron Microscope and EDAX.

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