Electrochemical reduction of CO₂ on Ni (OH)₂ doped water dispersible graphene under different electrolyte conditions

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Abstract

Association of the cathodic operation of Ni(OH)₂ doped water dispersible graphene (WDG) nanocomposite with three different electrolytes (NaHCO₃, KHCO₃, and NaCO₃) with the help of carbon dioxide (CO₂) electrochemical reduction is presented in this research. Graphene in short time is effectively synthesized and Ni(OH)₂ doped on WDG by electrochemical method, structure, morphology and characterization analysis by X-ray diffraction, scanning electron microscope, transmission electron microscope and Raman spectroscopy. CO₂ is effectively reduced to carbon monoxide (CO) at enhanced situation. Fourier transform infrared spectroscopy, which is used to exanimate integrated Ni(OH)₂-WDG nanocomposite surfaces so as to uncover the carbonate ions and CO during reduction at three different electrolytes. The electron charge resistance of the nanocomposite is investigated by using electrochemical impedance spectroscopy analysis. Analysis of the Ni(OH)₂-WDG nano composite was performed to decouple electrochemical reduction processes of CO₂ to CO at different electrolytes by cyclic voltammetry and linear sweep voltammetry.

Keywords CO₂ · Reduction · Carbon dioxide · Electrochemical · Cyclic voltammetry · Linear sweep voltammetry

1 Introduction

Although, CO₂ plays a significant part in producing greenhouse effect, it is accountable for the warming of the Earth [1–3]. CO₂ is emanated, while performing human activities such as deforestation, fossil fuels combustion, and industrial processes. One must follow most of the valuable methods for reducing CO₂ emissions, i.e. to diminish the consumption of fossil fuels. In current times, the ratio of atmospheric mixing of CO₂ is higher than what it was in the last 800,000 years [4–10]. In the nineteenth century, a chemical scheme of converting CO₂ and hydrogen (H₂) to methane was developed and later the same was transformed to liquid fuels [6]. For the production of gases like carbon monoxide (CO)/H₂ and other supportive organic compounds like methanol, methane, ethylene, and formic acid, CO₂ was utilized as the C1 feedstock. The organic compounds have been merged with numerous chemical,

photochemical, biochemical, and electrochemical procedures [8–10].

Owing to several reasons, the conversion of using CO₂ electrochemical catalysis methods enticed a great deal of attention among researchers. Let us take a look at these reasons: (1) by means of electrode potentials and reaction temperature, the method is controllable; (2) the supporting electrolytes can be totally reprocessed, so as to minimize the whole chemical utilization to simply water (or) waste water; (3) the electricity utilized to drive the method can be attained without producing any new CO₂-sources; and (4) The electrochemical reaction systems are compressed, modular, on-demand, and simple to scale-up [11]. In the past decades, the electrochemical CO₂ reductions at metals (e.g. Hg, Cu, etc.) and related electrodes in addition to electrocatalytic CO₂ reduction have been extensively examined in aqueous and non-aqueous Media [12–18].

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Carbon materials incorporates glassy carbon, graphite, boron-doped diamond (BDD), carbon black, carbon nano fiber, carbon tubes (CNTs), and these days graphene is extensively used as an electrode in the elementary innovations and application aspects of electrochemistry and electro analysis [19, 20]. Ni(OH)₂/graphene composite has proven its application in energy storage applications like supercapacitor owing to its high specific capacitance of graphene, energy density, and good cyclic stability [21, 22].

In this paper, graphene is synthesised through electrochemical technique and then graphene is converted to WDG. In addition, Ni(OH)₂ is doped on the surface on WDG with the help of electrochemical techniques. The cathodic performance of Ni(OH)₂-WDG composite at three different electrolytes, namely, NaHCO₃, KHCO₃, and NaCO₃ are investigated in detailed manner.

2 Experimental

2.1 Preparation of graphene

The graphene was made with the help of electrochemical process. The graphite rods were treated both as an anode and cathode by distributing at a distance of 2 cm in 3 M intensity of H₂SO₄ mixture. This mixture was used as an electrolyte. The graphene was washed from the graphite rod by escalating a potential of more than 7 V through DC electrical power supply. The acquired graphene was blended with the electrolyte mixture. The pure graphene was separated from the solution by several exfoliating with the help of double distilled water.

2.2 Preparation of water dispersible graphene

Graphene powder (0.1 g) was dissolved in 100 mL purified water and sonicated. Furthermore, 0.5 M NaOH is added to the solution drop wise and pH was altered to above 8. Additionally, the mixture was dehydrated at 80 °C to attain powdered mixture [23].

2.3 Ni (OH)₂ doped water dispersible graphene

Ni(OH)₂ was effectively doped on WDG by using electrophoretic deposition (EPD). The conductive substrate such as stainless steel (SS) is used as negative electrode during the EPD procedure. The substrate was rinsed by ultrasonic vibrations caused in acetone, ethanol, and deionised water, correspondingly. The positive counter electrode was Pt with the same elements. Prior to EPD, the WDG and NiCl₂ in 50 mL of deionised water were ultrasonically spread for 2 h. The electrodes were in the gap of 10 mm

and immersed in the colloidal solution saturated with nitrogen gas. An applied potential of 2–10 V was used for 30–500 s to deposit. EPD was carried out on a current–voltage monitor and the current accuracy of 13 mA, when the applied voltage came to 10 V. After EPD, the nanocomposite film was dehydrated at 80 °C in an oven overnight.

2.4 Materials characterization

With the help of CuK_α ($\lambda = 1.5406 \text{ \AA}$) as a radiation source, the phase and crystalline nature of the synthesised samples were examined by X-ray diffractometer (XRD) (X'Pert PRO, PANalytical, The Netherlands). The samples were examined over the 2θ range of 10–80 °C at room temperature (298 K). In relation to the reference diffraction data, the observed peak positions and the relative concentration of the powder pattern were indexed. The surface morphology of WDG and Ni(OH)₂-WDG were decided by means of a scanning electron microscope coupled with energy dispersive X-ray analysis (SEM-EDAX) (JEOL JSM-6390LV, Japan) at 20 kV with a magnification of 10000× at 1 μm scale. Functional group information about powder surface was examined by means of FTIS (Spectrum 100; PerkinElmer, USA). The spectra were collected in the range of 4000–500 cm^{-1} .

2.5 Electrodes preparation and characterization

The SS plate was sliced into small pieces (16 cm^2) and later on buffed delicately with the help of a solvent (acetone). The synthesised Ni(OH)₂-WDG nanocomposites powder was assorted with a polyvinylidene difluoride (PVDF) at a ratio of 85:15 in a small quantity of *N*-Methyl-2-pyrrolidone as a solvent to make a paste. The paste substance was covered over the separate SS plates by means of a doctor blade [24]. The coating was done repetitively multiple times so as to attain a uniform thickness (10 μm) of electrodes on the SS plates. The Ni(OH)₂-WDG nanocomposites electrodes were dehydrated at 85 °C in a hot-air oven for about 1 h and then used for further examination. The method of electrolysis was handled in the terylene diaphragm cell of 100-mL volume. The anode was an SS net (16 cm^2) and cathode was an Ni(OH)₂-WDG electrode (16 cm^2). The gap between the anode and cathode was 2 cm. The electrical power was presented by a laboratory direct current power supply with a current–voltage monitor.

The nitrogen gas was passed into the electrolyte for 30 min so as to eliminate O₂, and CO₂ gas that was passed into the electrolyte for 30 min before the reaction takes place. NaHCO₃ (1 M) was selected as the electrolyte at room temperature thereby keeping the voltage at 4 V. Similar procedure was done for another two different

electrolyte (KHCO_3 and NaCO_3) at as prepared the two Ni(OH)_2 -WDG electrodes. During the preparative electrolysis, a sample was taken (in 10 min-periods). At a low current density of 8 mA/cm^2 , Ni(OH)_2 -WDG electrodes could function. A schematic diagram is given in Fig. 1.

2.6 Electrochemical measurements

The CV and EIS behavior of Ni(OH)_2 -WDG nanocomposites electrode was investigated with the help of a three-electrode cell set-up. In this set-up, the Ni(OH)_2 -WDG was used as a working electrode, where as platinum (Pt) and saturated calomel were majorly used as the counter and reference electrodes, correspondingly, for the carbonate-based electrolytes. The CV analysis was done in Ni(OH)_2 -WDG at different electrolytes in fixed scan rate by means of Autolab equipment (PGSTAT302 N, Metrohm Autolab, and the Netherlands). The applied potential window for CV study was -1 – 1 V at 10 mV/s scan rate. The present performance of cathode was determined from the extrapolated data of the CV test.

3 Results and discussion

3.1 Structural characterizations

Figure 2a demonstrates XRD patterns of the WDG sheets, a sharp peak at 26.3° (002). The peak experimented in 26.3° is attributed to the crystal nature of the WDG [23].

Figure 2b explains XRD patterns of Ni(OH)_2 -WDG composite, demonstrating that the Ni(OH)_2 -WDG compound has been well-synthesised, peaks at 12.1 , 26.3 , 33.3 , and 54.4° relating to the (003), (002), (101), and (110) diffraction peaks correspondingly [25]. Figure 3 in Raman spectra, the D, G, and 2D bands are evidently seen in 1343 , 1575 , and 2704 cm^{-1} , in that order, for the WDG sample. This is owing to the in-plane band stretching motion of pairs of sp^2 hybridization. The aforementioned examination assures the presence of a graphene monolayer [26].

The morphology and structure of WDG and Ni(OH)_2 -WDG nanocomposites were explained with the help of SEM and TEM which are demonstrated through Fig. 4A and B. The SEM and TEM that gives a clear sign for the transparency of the WDG implies a thin film over the entire substrate and the Ni(OH)_2 well doped on WDG surface.

3.2 FTIR of FeTiO_3

The typical FTIR spectra of Ni(OH)_2 -WDG exclusive of electro reduction and Ni(OH)_2 -WDG electrode surface after electro reduction at three different electrolytes is shown in Fig. 5a–d, respectively. Graph (a) clarifies synthesized Ni(OH)_2 -WDG had four important peaks at 538 , 1347 , 1452 , and 1657 cm^{-1} . The absorption peak 538 cm^{-1} is due to Ni-OH is stretching for Ni(OH)_2 , 1347 , 1452 , and 1657 cm^{-1} owing to the C–H (rack), C–H (bend) and C=C for WDG [26, 27]. Graph (b), (c) and (d) elicited after CO_2 reduction in three different electrolytes (NaHCO_3), (KHCO_3), and

Fig. 1 Schematic diagram for electrocatalytic reduction of carbon dioxide on Ni(OH)_2 -WDG at at three different electrolytes

Fig. 2 (a) XRD patterns of WDG. (b) XRD patterns of Ni(OH)₂-WDG nano composite

(NaCO₃) Ni(OH)₂-WDG electrodes surface. Graph (b) and (c) had four new peaks that were found (698, 834, 996, and 1929 cm⁻¹) due to the C-H, C-H (bend), O-H (carboxylic acid), (C=O) than graph (a) graph (d) for NaCO₃ electrolyte after reduction Ni(OH)₂-WDG surface was not clear, new peaks obtain than graph (a). After CO₂ reduction, more sharp carbonyl functional group adsorption was found on Ni(OH)₂-WDG in NaHCO₃ and KHCO₃ electrolytes than NaCO₃ electrolyte.

3.3 Electrochemical impedance spectroscopy

The Nyquist plots of Fig. 6 explain the charge transfer resistance analysis of the Ni(OH)₂-WDG nanocomposite at only electrolytes (1 M NaHCO₃, KHCO₃ and NaCO₃). Red color line specifies NaHCO₃, blue line indicates KHCO₃, and

Fig. 3 Raman spectrum of WDG

green line denotes NaCO₃. This graph gives a clear picture that NaHCO₃ electrolyte medium favour high electron charge transfer that occurs on Ni(OH)₂-WDG composite electrode surface than KHCO₃ and NaCO₃ electrolyte medium. The HCO₃⁻ and Na⁺ electrolyte medium favours the low resistance on Ni(OH)₂-WDG mixture.

3.4 Cyclic voltammetry

The CV of Ni(OH)₂-WDG at three different CO₂ saturated electrolytes (1 M NaHCO₃, KHCO₃, and NaCO₃) were done. Cathodic behaviour of as prepared Ni(OH)₂-WDG nanocomposites were compared at three different CO₂ saturated electrolytes. Calomel electrode was used as reference electrode and Platinum electrode was used as counter electrode. CV study of Ni(OH)₂-WDG due to N₂: CO₂ saturated in three different electrolytes (1 M NaHCO₃, KHCO₃ and NaCO₃) at 10 mV/s scan rate at room temperature was done. As shows in Fig. 7 CV for Ni(OH)₂-WDG composite at CO₂ saturate at three different electrolytes (1 M NaHCO₃, KHCO₃ and NaCO₃). The clear reduction peaks were observed between -0.5 and -0.4 V, that should result from one-electron reduction of CO₂, which generated an anion radical of CO₂ [28].

This anion radical, however should react rapidly with the intermediate at the desired product. Graph (a) indicates CV for Ni(OH)₂-WDG in CO₂ saturated at 1 M NaHCO₃ electrolyte, graph (b) shows CV for Ni(OH)₂-WDG in CO₂ saturated at 1 M KHCO₃ electrolyte and graph (c) depicts CV for Ni(OH)₂-WDG in CO₂ saturated at 1 M NaCO₃ electrolyte. In CV reduction peaks, positive site shifted depending on electrolyte serial (NaHCO₃, KHCO₃ and NaCO₃). Increasing the cathodic behavior of Ni(OH)₂-WDG in CO₂

Fig. 4 **A** SEM image of WDG, **B** TEM image of WDG (**a**) and Ni(OH)₂-WDG (**b**) nano composite

Fig. 5 FTIR of The graph (**a**) Ni(OH)₂-WDG, graph (**b**), (**c**) and (**d**) after CO₂ reduction for Ni(OH)₂-WDG electrodes surface at three different electrolytes (1 M NaHCO₃, KHCO₃ and NaCO₃)

saturates NaHCO₃ than KHCO₃ and NaCO₃ electrolytes. These CV results indicate that electrolyte plays an

Fig. 6 Electrochemical impedance spectroscopy of Ni(OH)₂-WDG electrodes surface at three different electrolytes (1 M NaHCO₃, KHCO₃ and NaCO₃)

important role in CO₂ electrochemical reduction and HCO₃⁻ ions also offers great help in the CO₂ reduction process.

The K⁺ ions, increasing the cathodic behavior and increasing reaction intermediated for CO₂ to CO [29], this CV results represents that the Na⁺ ions increases the cathodic behavior than K⁺ ions in electrolyte medium. The

Fig. 7 The CV of Ni(OH)_2 -WDG at three different CO_2 saturated electrolytes **a** NaHCO_3 , **b** KHCO_3 and **c** NaCO_3

Na^+ ions are well coordinated to the intermediate components of the CO_2 electrochemical reduction.

3.5 Linear sweep voltammogram

LSV is one of the electrochemical studies for the reduction of CO_2 . Figure 8 gives a clear explanation that the mixture of Ni(OH)_2 -WDG nanocomposite on reduction of CO_2 at different electrolytes (1 M NaHCO_3 , KHCO_3 and NaCO_3), high efficiency reduction peak can be seen between -0.5 and -0.4 V. A, blue line specified NaHCO_3 electrolyte peak appear near to -0.4 V, red line demonstrates KHCO_3 electrolyte peak show near to -0.5 V and green line signifies NaCO_3 electrolyte peak that appear above -0.5 V. The outcome specified to well evidence that NaHCO_3 electrolyte is of great help to CO_2 reduction of Ni(OH)_2 -WDG nanocomposite. Figure 9 tafel plot for LSV of Ni(OH)_2 -WDG nanocomposite reduction of CO_2 at different electrolytes (1 M NaHCO_3 , KHCO_3 , and NaCO_3). This figure gives a clear view of Ni(OH)_2 -WDG composite reduction peak that occurs near -0.4 V and better CO_2 reduction behavior than Ag, Pt, and Ru doped TiO_2 and Cd, Co (-0.75) [30].

Fig. 8 Linear sweep voltammogram of Ni(OH)_2 -WDG at three different CO_2 saturated electrolyte (1 M NaHCO_3 , KHCO_3 and NaCO_3)

Fig. 9 Tafel plot for linear sweep voltammetry of Ni(OH)_2 -WDG at three different CO_2 saturated electrolyte (1 M NaHCO_3 , KHCO_3 and NaCO_3)

4 Conclusions

The electrolysis researches were transmitted out in an undivided cell under mild conditions; prevent the adding up of toxic solvents and catalysts. The electrical power was provided by a laboratory direct current power supply with a current-voltage monitor. Ni(OH)_2 -WDG mixture could be functioned at low current density $8 \text{ (mA/cm}^2\text{)}$ attained with the help of electrode for CO_2 reduction at three different electrolytes. XRD specifies good crystalline peaks that exist by effective fusion of WDG. When doped Ni(OH)_2 on WDG, it has fully reduced the crystalline structure of WDG and it is well indicated in the XRD for Ni(OH)_2 -WDG. Raman, SEM, and TEM images signifies WDG had monolayer by effectively blended WDG, another SEM and AFM images epitomizes the white portion point to the Ni(OH)_2 fine doped on WDG. FTIR indicates adsorbed carbonyl functional groups on Ni(OH)_2 -WDG at three different electrolytes (NaHCO_3 , KHCO_3 , and NaCO_3) after CO_2 reduction, increased concentration peaks appear NaHCO_3 than KHCO_3 and NaCO_3 electrolytes on Ni(OH)_2 -WDG electrode surface. The results of CV and LSV specifies the good cathodic behavior of Ni(OH)_2 -WDG composite in CO_2 reduction than Cd, Co, and Cu (-0.75), this consequence epitomizes Ni(OH)_2 -WDG has better CO_2 reduction behavior (-0.4 V) in NaHCO_3 than the KHCO_3 and NaCO_3 , Na^+ and HCO_3^- ions augments the CO_2 reduction cathodic behavior of Ni(OH)_2 -WDG electrode.

Compliance with ethical standards

Conflict of interests The authors declare that they have no conflict of interest.

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