Investigation of graphene-based nanocomposite for hydrogen storage

S J Baloyi 1,*, A Ngqalakwezi 1,2, D Nkazi 2 and T A Ntho 1

1 Advanced Materials Division, Mintek, Private Bag X3015, Randburg 2125, Southern Africa

2 School of Chemical and Metallurgical Engineering, Wits University, Braamfontein, South Africa

E-mail: jeffreyb@mintek.co.za

Abstract. In this study, a simple, fast, and green one-pot method was developed for the preparation of Ni/Graphene nanocomposite for the storage of hydrogen. The precursor graphene oxide was prepared from expanded graphite flakes using a modified Hummer’s method. Graphene oxide was reduced effectively using natural reducing agents such as lemon juice as eco-friendly potential reducing agents instead of harmful hydrazine (N₂H₄). The characterization of as-synthesized graphene oxide and Ni/graphene nanocomposites were performed by powder X-ray diffraction (p-XRD), high-resolution electron microscopy (HRSEM) with energy dispersive spectroscopy (EDS) analysis and transmission electron microscopy (TEM) before investigating the performance for hydrogen storage. It was observed from the results obtained that the synthesized graphene contains thin stacked flakes of shapes having a well-defined multi-layered structure at the edge. And the round shaped Ni nanoparticles of 13 nanometres in size were dispersed around the graphene structure. The hydrogenation capacity of the Ni/graphene nanocomposites were tested using thermogravimetric analysis (TGA). The prepared Ni/graphene nanocomposites exhibited good hydrogen storage capacities.

1. Introduction

The heavy use of carbon based material and their negative effects on the atmosphere have pushed the world into a paradigm shift where greener systems and methods have to be implemented. Environmental issues like global warming and acid rain are direct consequences of using fossil fuels, as a result, intensified research to find more environmentally friendly sources of energy and in the long run, eradicate the current environmental issues have been prioritized. The use of hydrogen as a substitute source of energy has gained favorable consideration because of its minimal emissions to the environment [1-3]. Hydrogen can form solid through physical or chemical combination with materials like complex hydrides, carbon materials, and metal hydrides. The United States Department of Energy requires these materials to have high volumetric and gravimetric densities at low temperatures and pressures [4]. Metal hydrides garnered a lot of attention due to their high gravimetric hydrogen capacities however their slow kinetics have hindered the practical application of these materials for hydrogen storage. Carbon materials have restricted hydrogen uptake due to weak Van Der Waals forces. However, researchers have suggested that decorating these materials with metal nanocrystals could improve hydrogen uptake in these materials [5].

Graphene amongst other material has been considered as a potential material for hydrogen storage because of its excellent onboard reversibility, high specific surface area, lightweight characteristic, and chemical stability. Graphene is a 2D carbon material with a 2sp honeycomb lattice structure [6]. Graphene is a very versatile material as such it can be manipulated to form hybrid materials by
integrating it with nanomaterial. Hybrid materials are achieved through the decoration of the surface with metal nanocrystals resulting in improved catalytic activity and good electrochemical properties. Chen et al. [7] have reported success in attaching platinum, iron, and palladium onto the surface of Graphene. Zhou et al. [5] suggested that Ni makes the sorbent structure stable by re-arranging the geometry of graphene to catalytically improve the hydrogenation and dehydrogenation reaction in nanocomposites. In addition, reduced graphene oxide decorated with Ni shows improved cycling performance.

In this work, we synthesized Ni/Graphene nanocomposites, with precursor graphene prepared using Modified Hummers method and reduced with eco-friendly reducing agents. It was noted that the uptake of hydrogen is relatively proportional to the pressure of hydrogen.

2. Experimental procedures

2.1. Materials and chemicals

Nickel (II) acetate tetrahydrate (Ni [(OAc)₂]₃) and expandable graphite flakes (99.99%, 200 mesh) used to prepare graphene oxide was purchased from Sigma Aldrich. Lemon juice that was used as a natural reducing agent to reduce graphene oxide to graphene was purchased from Woolworth retailer store. Analytical grade potassium permanganate (KMnO₄), concentrated sulphuric acid (98%), hydrogen peroxide aqueous solution (H₂O₂) (30%), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from Merck Chemicals (Pty) Ltd. All chemicals were utilized as such without further purification. High purity water (resistivity 18.2 MΩcm) decontaminated using a Milli-Q water system Millipore in the Mintek laboratory was used to prepare all aqueous solutions throughout.

2.2. Preparation of graphene oxide and graphene

Graphene was prepared from graphene oxide (GO) by reduction of graphene oxide using a natural reducing agent such as lemon. Therefore, GO was prepared first from natural expandable graphite flakes using a modified Hummers method. In a typical preparation, approximately 3 g of expandable graphite flakes were added into concentrated H₂SO₄ (70 mL) and stirred while the temperature was kept low at 10 °C in a beaker with ice water. KMnO₄ (9 g) was slowly added to the mixture while stirring at a constant speed. The temperature was raised to 35 °C, after the complete addition of KMnO₄ and stirred for a further 30 min. The mixture was diluted with high purity water (150 mL) and the temperature was raised to 95 °C. Additional high purity water (500 mL) and 30% H₂O₂ (20 mL) were added to the mixture (producing a dark brown to the yellow mixture). The H₂O₂ solution was consequently added to the mixture to stop the reaction. The obtained graphite oxide was exfoliated to GO through sonication in water for 10 min at room temperature. The subsequent mixture was washed with 15 mL of 1M HCl aqueous solution to remove metal ions and centrifuged at 4000 rpm for 30 minutes. The mixture was added to 5000 mL of high purity water and left stirring overnight. Then followed by filtering and washed again to further remove acid then oven-dried overnight at 30 °C. The solid obtained was then reduced with lemon juice as an environmentally friendly natural reducing agent.

2.3. Preparation of graphene-based nanocomposite

Ni/Graphene nanocomposite was prepared from precursor graphene oxide prepared by a modified Hummers method. Nickel (II) acetate tetrahydrate and graphene oxide gel were utilized as starting materials at a ratio of 5%:95% Ni to C atomic ratio. Typical, about 2.51 g of (Ni [(OAc)₂]₃) were disintegrated in 50 mL of high purity water. The (Ni [(OAc)₂]₃) mixture was added into 20 mg/mL of graphene oxide gel. The mixture turned a dark shade of brown and was stirred for a few minutes before being ultra-sonicated for 10 min at 25 °C to attain a homogenous solution. Exactly 10 mL of lemon juice was slowly added to the mixture. The pH of the mixture was maintained at 10-12 through the addition of 1M NaOH solution while stirring. The solution was stirred again for 10 min before the mixture was placed in a tightly closed container and heated at 70 °C for 60 min, then after the heating was raised to 95 °C for another 60 min. Subsequently, the uniform solution was centrifuged and the remaining contaminants were washed repeatedly with high purity water and centrifuged again. Then the obtained precipitate was vacuum dried to yield a powder of Ni(OH)₂/graphene precursor. Lastly, the Ni(OH)₂/graphene was reduced to Ni/graphene nanocomposite by hydrogen thermal treatment with hydrogen at 350 °C for 3 h.
2.4. Characterization

X-ray diffraction (XRD) patterns were obtained by a high-resolution Bruker AXS D8 X-ray advanced powder diffractometer with CuKa-radiation (40 kV, 40 mA, 1.78897 Å) using a LinxEye detector. The XRD patterns were recorded with a step size of 0.02° in the 20 range of 5 to 80° diffraction angle and using a standard speed with an equivalent counting time of 1 second per step. The specific surface area (SBET) was calculated by the Brunauer-Emmett-Teller (BET) method, using the Micromeritics ASAP TriStar 3000 unit, which operates with physical adsorption of a monolayer of nitrogen gas (area = 0.162 nm2) at −196 °C and at a pressure of about 2 µmHg for porosity measurement. HRTEM images were obtained using a JEM2100F electron microscope from JEOL, Ltd. fitted with an EDX, wavelength dispersive spectroscopy (WDS) and electron beam backscattered diffraction (EBSD) operating on Oxford Instruments software. The instrument was operated at an accelerating electron beam of 120 kV. The images were photographed using a Proscan CCD camera and image analysis was done using the Soft Image System (SIS) software. Samples were prepared by suspending the powder in methanol and applying the suspension to a carbon coated copper grid. Elemental analysis of Ni/graphene was performed using an EDX equipped with TEM. The samples were then allowed to dry at 25°C and the grid viewed under the microscope. The Raman characterization of the samples was conducted using a PerkinElmer Raman spectroscopy with a wavelength of 785 nm laser. The lateral resolution was measured at ~1 µm. An accumulation time of 3 seconds with a grip spacing of 0.25 mm was used in the mapping of each spot in the sample. The PerkinElmer (Bucks, UK) spectrum software was utilized to process the spectra.

2.5. Hydrogen storage

The hydrogen storage uptake of Ni/graphene was analyzed using high-pressure autoclave made of stainless steel and simultaneous thermogravimetric analysis (STA 6000; Perkin–Elmer model). The sample inside high-pressure autoclave reactor was charged with hydrogen at different pressures (0 bar, 5 bar, and 10 bar) and standard temperature. The reaction temperature inside the reactor was measured using a thermocouple and controlled by a PID regulator. The samples were each charged with hydrogen for 30 min and then placed in a firmly sealed container at room temperature for TGA analysis. Approximately 5 - 10 mg of the sample weight was used, the sample was kept for 10 min at 20 mL/min and then heated at a regular increase of temperature from 25°C to 900°C with a heating rate 10°C/min while the nitrogen flow rate was 20 mL/min. Hydrogen release was measured with an increase in temperature. A hydrogen storage capacity in the sample was calculated from the weight percentage of the sample which was taken as a function of temperature. The sample not charged with hydrogen (0 bar) was used as a reference to quantify for other oxidation products, possible water adsorption and other impurities and other oxidation products that might have been attached to the sample during the transfer step.

3. Results and discussion

3.1. Oxidation reaction color change

There was an observable change in the color of expandable graphite blend during the oxidation reaction. The dark green color of the graphite blend was observed before oxidation reaction and the graphite blend became dark brown to bright-yellow in color after oxidation reaction. The dark green color before oxidation reaction might be attributed to contact between H2SO4 and Mn2O7 from KMnO4 used as starting material. At room temperature, Mn2O7 appeared as dark red oil before contacting H2SO4. The Mn2O7 result from a reaction between reaction KMnO4 and H2SO4 as illustrated in Eq. (1).

\[ 2\text{KMnO}_4 + 2\text{H}_2\text{SO}_4 \rightarrow \text{Mn}_2\text{O}_7 + \text{H}_2\text{O} + 2\text{KHSO}_4 \]  

(1)

Then the subsequent dark brown to bright-yellow suspension was terminated by addition of more high purity water followed by hydrogen peroxide solution.

3.2. Physiochemical and morphological characterization

Transmission electron microscopy (TEM) is used to produce sample images by scanning with a focused electron beam. Sample images are taken by a beam of electrons transmitted through a sample which
interacts with the sample and forms an image. Figure 1a-d shows the TEM images of the Ni(OH)$_2$/graphene before reduction as a reference and the surface morphologies of the precursor material after reduction. The particles size of the Ni(OH)$_2$ on the graphene were observed to have an average size between 23 - 70 nm. After the thermal reduction of Ni(OH)$_2$/graphene to Ni/graphene using hydrogen, the Ni particles in Ni/graphene nanocomposite were homogenously dispersed over the graphene surface with a mean particle size of about 13 nm. The result of chemical analyses of the Ni/graphene shown in Table 1 indicates a successful preparation of Ni/graphene nanocomposite. Table 1 reveals the presence of C (86%), O (10.29%) and Ni (4.58%) on the Ni/graphene surface, which correspond to the component ratio used for the preparation. The BET surface area of graphene was found to be 711.2 m$^2$/g with adsorption pore width of 5 nm.

Table 1. Chemical analysis of Ni/graphene sample.

| Sample       | C (%) | O (%) | Cu (%) | Cl (%) | Ni (%) | Total (%) |
|--------------|-------|-------|--------|--------|--------|-----------|
| Ni/Graphene  | 86    | 10.29 | 0.08   | 0.27   | 4.58   | 100       |

Figure 1. TEM images at 100 nm and 200 nm of (a & c), Ni(OH)$_2$/graphene and (b & d), Ni/graphene.

The XRD characterization gives an indication of the phase composition, crystal structure of materials and interlayer distance between graphene oxide and graphene. This analysis technique is based on Bragg’s law [5]. Figure 2(a) indicates the XRD patterns of graphene, graphene oxide, and graphite. While Figure 2(b) shows a Ni/graphene before and after reduction and metallic Ni. Figure 2(a) demonstrates that graphite exhibited a sharp and high-intensity diffraction peak at $2\theta = 31^\circ$. The interlayer distance ($d$-spacing) of 0.33 nm along the (002) orientation was obtained. The graphite peak completely disappears when oxidation has taken place as can be observed from the red and blue lines representing graphene and graphene oxide respectively. As shown in Figure 2(b) after hydrogen thermal reduction, the complete disappearance of the Ni(OH)$_2$ peak ($2\theta = 30.2^\circ$) in the Ni/graphene (black line) indicates that it was reduced to Ni in the graphene structure. Three diffraction peaks can be observed in the diffraction patterns Ni (blue line) at $2\theta = 52.8^\circ$, $61^\circ$ and $93^\circ$, which corresponds with the decrease peaks of Ni/graphene (black line) diffraction pattern. Again this results confirm the successful reduction of Ni(OH)$_2$ to Ni in the graphene surface. These results suggest that lemon juice successful reduced graphene oxide to graphene. Other researchers proposed three possible routes for reduction of O group from graphene oxide; epoxide from graphene oxide are reported to be attacked by lemon juice from back side of the epoxide ring, the sp$^3$ C can be attacked by lemon juice from the front side of the epoxide ring and the sp$^2$ C at the meta position of epoxide can be attacked by lemon juice [7].
3.3. Electronic structure determination

Raman spectroscopy identifies the vibrations of interatomic bonding and structure that come up due to structural differences [8]. This technique utilizes a monochromatic laser to make interactions with the phonons and molecular vibrational modes which leads to the laser energy being moved up and down through inelastic scattering [9]. For the graphene structure, the D and G bands are the principal characteristics in the spectrum. The G represents and includes sp² hybridized carbon in plan vibrational mode while the D band represents carbon hybridized in the sp³ band as a defected band [8]. As shown in Figure 3, the D and G are located at 1578 cm⁻¹ and 1658 cm⁻¹ respectively. The Ni/graphene spectra depict no shift in the peak position however the Ni/graphene charged with hydrogen depicts a shift. From the Ni/graphene spectra, it can be observed that sp² hybridization was strengthened while the sp³ was weakened due to the decreased D/G intensity ratio. High-frequency peaks are proportional to the number of modes which increase as the number of graphene sheets increase thus low intensity peaks are caused by the packing of graphene platelets [10-1]. The restacking of the graphene platelets in the Ni/graphene charged with H₂ results in the shift of the D peak which can be observed in the spectra.
3.4. Hydrogen storage capacity of Ni/Graphene composite

Thermogravimetric analysis was used to verify the hydrogen uptake and release in as-prepared Ni/Graphene. The sample was heated at a rate of 10°C/min under nitrogen conditions. A non-hydrogen charged sample was first run as a reference for verifying hydrogen uptake in Ni/Graphene sample charged at 5 and 10 bars respectively. The non-charged Ni/Graphene sample had a lower mass loss compared to the charged sample due to the eradication of gas impurities on the sample and adsorbed moisture. The hydrogen charged samples showed a faster decrease in mass with increasing temperature as depicted from Figure 4. A continuously decrease in a weight loss for hydrogen charged samples with an increase in hydrogen charging pressures were observed. Zhou et al. [4] reported on the characteristics that could affect the mass changes of the samples charged with hydrogen when using TGA: elimination of gas toxins and adsorbed water during the transfer process, hydrogen release and the reduction of hydrogen in NiOx, removal of water that resulted from the potential of the hydrogen oxidizing due to the existence of Ni particles during the transfer step and an irreversible interaction between Ni/graphene nanocomposite and hydrogen upon thermal treatment [11 12]. Therefore, these assumptions were considered when calculating the hydrogen storage capacity using uncharged nanocomposite as a reference. Typical, the amount of released hydrogen was calculated by subtracting the weight loss of the uncharged sample (0 bar) from weight loss of each sample charged with hydrogen [13]. The Ni/graphene nanocomposite takes up hydrogen with a capacity of 0.25 wt% at standard temperature and at standard pressure of hydrogen. The hydrogen storage capacity increased with an increase in hydrogen charging pressure to 10 bar, the hydrogen storage capacity reached 2.78 wt% in the Ni/graphene nanocomposite.
Figure 4. TG analysis of hydrogen uptake in the Ni/graphene nanocomposites with a loading amount of 5 at. % Ni at different hydrogen charging pressures (5 and 10 bar).

4. Conclusions
The Ni/graphene nanocomposites were successfully prepared for hydrogen storage using a natural environmental friendly reducing agent. It was demonstrated in this study that lemon juice can efficiently reduce graphene oxide to graphene. This method can be considered as eco-friendly and environmental friendly since the method used one-pot preparation process and natural reducing agent. The Ni/graphene nanocomposite achieved a hydrogen storage capacity of 0.25 wt. % at standard temperature and standard hydrogen charging pressure. The amount of hydrogen stored in the Ni/graphene nanocomposite was found to be directly proportional to the hydrogen charging pressure. The hydrogen gravimetric density of 2.78 wt. % was achieved with Ni/graphene nanocomposite charged with hydrogen at 10 bar. The morphologies of nanocomposites will be studied further by using a scanning electron microscope (SEM). Auto Chem connected to mass spec will be used to support claims made using TGA as mass spec can give exact type of gas being released in the nanocomposite. Furthermore, a high-pressure volumetric analyzer (HPVA) will be used to determine hydrogen storage capacity.

Acknowledgment
The authors wish to acknowledge financial support from the Mineral Science Council of South Africa (Mintek), South Africa through research Grant ADR 31901.

References
[1] Schlapbach L and Züttel A 2001 Nature. 414 353
[2] Wagemans RW, van Lenthe JH, de Jongh PE, Van Dillen AJ, K. de Jong 2005 J Am Chem Soc. 127 16675
[3] Xu E, Li H, You X, Bu C, Zhang L, Wang Q, Zhao Z 2017 International Journal of Hydrogen Energy. 1 6
[4] Zhou C, Szpunar J.A., Cui X 2016 Applied materials and interfaces. 8 15232
[5] Chong S.W., Lai C.E., Hamid S.B.A 2015 Ceramics International. 41 9505
[6] Chen M-L, Park C-Y, Choi J-G, Oh W-C 2011 Journal of the Korean Ceramic Society. 48 147
[7] Kim Y, Lee J, Yeom M.S, Shin J.W, Kim H, Cui Y, Kysar J.W, Hone J, Jung Y, Jeon S 2013 Nature Communications. 4
[8] Wall M 2012 Adv. Mater. Process. 170
[9] Gardiner DJ 1989 Springer. 1
[10] Childres L, Jauregui L.A., Park W, Cao W, Chen Y-P 2013 Development in Photon and Materials Research. 978
[11] Thakur S, Karak N 2012 Carbon. 50 5331
[12] Thomsen C, Reich S 2000 Phys. Rev. Lett. 85 5214
[13] Zhou C and Szpunar J.A 2016 ACS Applied Materials & Interfaces. 8 25933