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Electrophoretic Deposition of Nickel Decorated Multi-Walled Carbon Nanotubes for Hydrogen Gas Production

Prem Dangi, Jaya Prasad Bhatt, Sabita Shrestha*
Central Department of Chemistry, Tribhuvan University,
Kirtipur, Kathmandu, Nepal

Abstract: Electrophoretic deposition (EPD) is one of the very promising techniques being developed for manipulating CNTs and other Nanomaterials. This paper reports, the EPD of Ni-decorated MWCNTs for application in hydrogen gas productions. Hydrogen production is truly green technology which is used as a sustainable fuel in future as well as it has a great advantage for its eco-friendly production. Before deposition MWCNTs were purified and surface functionalized by conc. HNO_3. The oxidized MWCNTs were characterized by Fourier transfer infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). FTIR shows the presence of oxygenated functionalized group as –COOH on the surface of MWCNTs. The uniform EPD of MWCNTs is confirmed by SEM. EDS shows the presence of Nickel metal in Ni decorated MWCNTs as well as on the deposited substrates. The EPD experiments were carried out by using Ni-decorated MWCNTs on steel plate at 10V and 15V at a constant time of 6 min and a fix electrode distance of 1.5 cm. The evolution of hydrogen gas was carried out by a simple voltammetry cell via alkaline water electrolysis using 0.1M NaOH as electrolyte, where plane steel plate is used as anode and Ni-decorated MWCNTs deposited steel plate is used as cathode. The evolution of hydrogen gas at cathode and oxygen gas at anode is observed as expected. The hydrogen and oxygen was collected by downward displacement of water.

Keywords: Hydrogen production, Nickel decorated, Electrophoretic deposition

1. Introduction

Carbon Nanotubes (CNTs) are allotropes of carbon. CNTs are one dimensional carbon materials having the highest aspect ratio greater than 1000 [1]. Since the discovery of CNTs by Iijima, substantial research has been published which encountered enormous world-wide interest in this nanomaterial focusing in their physical and chemical properties.

The orientation between the graphitic hexagons and the nanotube axis i.e. helicity, the diameter, length of tubes and the crystalline quality are the agents which determine the properties of nanotubes [2]. Due to their excellent optical, electrical and mechanical properties, CNTs finds a wide range of applications in nanocomposites, biosensors, field emission devices, probe tips, catalyst support, supercapacitor etc [3]. Their wide ranges of applications are now forms a major interest of current research and development efforts.

One of the challenging task in CNT, is to manipulate CNT, individually or collectively, to produce a particular arrangement needed for a given applications. One very important technique to manipulate CNT is EPD [4]. EPD is a high level, versatile technique used to deposit colloidal suspension on to conductive substrate [5].

In recent time, EPD technique has been well-known due to its effectiveness, simplicity to handle and low cost to produce coating of controlled thickness and homogeneous microstructure with high packing density on a wide range of conducting substrates. The process allows the application of coating, thin and thick films, the shaping of bulk objects and the infiltration of porous substrates, fibrous bodies and textile structure with metallic, polymeric or ceramic particles [6].

EPD is accomplished through the movements of small charged particles dispersed in a suitable solvent, towards an electrode under the application of electric field [7].

Up to now, in best of our knowledge, there is no report on production of hydrogen gas by using electrode as metal decorated MWCNTs. This study investigated the effect of decorating the MWCNTs with Nickel nanoparticles on production of hydrogen gas via alkaline water electrolysis. The Ni–CNTs interaction induces an increase in the metallicity of the system as well as decoration of Nickel particles provides low-resistance ohmic contacts with CNTs [12], provide catalytic surface area to CNTs, high corrosion stability [13], high adsorption power etc [14]. It also provides improved quality in electrical and thermodynamic properties of CNTs.

Hydrogen gas shows a great potential as a fuel for a substantial energy.Hydrogen can be obtained in a large scale by water electrolysis. However, the cost and the energy consumption, which is directly proportional with cell voltage during the production of hydrogen gas by alkaline water electrolysis, are currently high, which can be minimized by reducing the over potential of the electrode reaction. This can be achieved by EPD technique, by making suitable deposited substrate, which consumes less energy [8]. Alkaline water electrolysis offers to low cost, sustainable and environmentally friendly as well as stability towards corrosion [9].

2. Materials and Method

2.1 Materials

MWCNTs (Iljin Nanotech. Co. Ltd. South Korea, purity >95%), synthesized by catalytic chemical vapor deposition (CVD) process were, used in this research work. Ethylene glycol, $NiCl_2.6H_2O$ were purchased from Qualigens (SQ) Chemical India. SDS from Hi-Media Laboratories Pvt. Ltd (Mumbai) India.All other chemicals HNO_3, NaOH are of AR grade and used as received.

2.2 Purification and Oxidation of MWCNTs

During the synthesis of Pristine Multi-walled carbon nanotubes, generally produce powders containing not only MWCNTs but also contains some impurities such as amorphous carbons, fullerenes, nanocrystalline graphite and transition metals that are used as catalyst during synthesis. These impurities sometimes hinder the accurate analysis of MWCNTs characteristics and limit the best performance of the MWCNTs applications to new functional devices. So they should purify before further treatment. In this work, pristine MWCNTs were purified/oxidized by refluxing in HNO_3 for about 4 hours. Purification removes the metallic catalysts, amorphous carbon and oxidation adds the different oxygen functional groups such as -COOH, OH^-, COO^- etc. on the surface [10, 11] of MWCNTs. The mixture was repetitively washed with distilled water until pH 7 and then filtered by using membrane filter paper having pore size 0.2 µm. The final black residue was then collected and dried in oven at 100 ºC for 1hr.

2.3 Deposition of Nickel Nanoparticles on the Surface of Oxidized MWCNTs

The deposition of Nickel nanoparticles was done on the surface of oxidized MWCNTs through wet chemical route using Ethylene Glycol as reducing agents. In this procedure, oxidized MWCNTs (0.051 g) were dispersed in ethylene glycol and 0.1 g of $NiCl_2$was added in that suspension. The pH of solution was adjusted to 9 by adding 2M NaOH and then the solution was heated with stirring. Finally the product was filtered by membrane filter paper of pore size 0.2 µm and washed with distilled water and dried in oven at 100 ºC for 1 hr.

2.4 Substrate Preparation

Stainless steel is used as a substrate for the electrophoresis process. In this process the stainless steels substrate were cleaved into 6 cm length and 5 cm breadth. Before EPD, the plates were mechanically and chemically cleaned to remove passive layers. Firstly, the plates were abaresing with silicon carbide paper ranging up to number 1000, 1500 and then finally 2000, then sonicated for 15 minutes and then dipped into the solution of hydroxide, phosphate and sodium carbonate at 50 ºC - 60 ºC for 15 minutes and then dipped into aqua-regia for 15 seconds. Finally, the plates were rinsed with distilled water and then dried in oven for 10 minutes [15].

2.5 Electrophoretic Deposition Process

Nickel decorated MWCNTs were used for the EPD process. For this Nickel decorated MWCNTs (0.027 g) were immersed in 50 mL D. I. water. Then 5 mL 1% sodium dodecyl sulfate (SDS) were added for well dispersion of MWCNTs and then sonicated for 6 hrs.

The electrophoresis process was performed on an experimental setup consisting of a DC power supply, electrolytic baths and two electrodes, one of which was the substrate for MWCNTs coating. Here, two steel plates were made anode and cathode. The inter-electrode distance was fixed at 1.5 cm for all experiments. The process was carried out for the constant time of 6 min using variable voltages as 5 V, 10 V, and 15 V. Following the deposition process, the samples were carefully taken out of the solution and dried in oven for 24 hrs.

The quality of deposited films could be easily seen through naked eyes. However the higher voltages i.e. 15 V produced more homogeneous and thick films of Ni-MWCNTs coating on the substrates. This plate was used for hydrogen production.

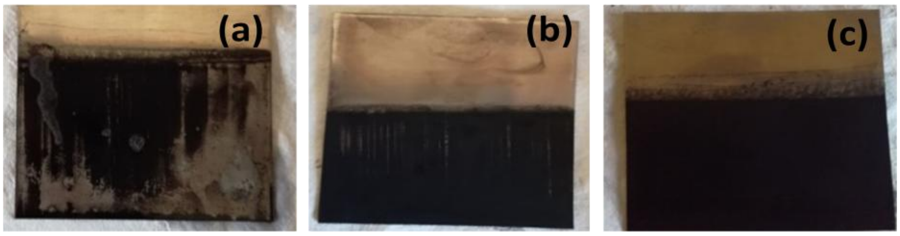

Fig 1. Images of electrophoretic deposited Ni-decorated MWCNTs (a) 5 V, (b) 10 V (c) 15 V respectively.

2.6 Production of Hydrogen Gas

The evolution of hydrogen gas was carried out by a simple voltammetry cell and collected by downward displacement of water.

When a D.C power supply (0-15V) is given, the decomposition of electrolyte occurs, forming gases i. e. oxygen and hydrogen which werecollected to respective collector. It is observed that, Hydrogen gas is collected at cathode side where as Oxygen gas is collected at anode side, as expected theoretically. The collected ratio is 2:1.

3. Measurements

The introduction of different functional groups on the surface of MWCNTs after acid treatment was obtained from ATR-FTIR Spectrometer (Shimadzu, IR-Prestige 21) at range 4000 - 400 cm^{-1}. The surface morphology of electrophoretic deposited films was examined by scanning electron microscopy (QUANTA FEG 250) with an acceleration voltage of 20 kV. Elemental composition was determined by energy dispersive spectroscopy X-Ray Fluorescence Spectrometer (EDX-GP ASSY EN 115V). A current–voltage characteristic or I–V curve (current–voltage curve) is a relationship, typically represented as a chart or graph, between the electric current through a circuit, device, or material, and the corresponding voltage or potential difference across it.Production of hydrogen gas, over potential and stability of voltammetry were analysis by current-voltage curve**.** In this work, BAK-1501T model no. of DC power supply is used.

4. Results and Discussion

4.1 Infrared Spectral Study

Fig. 2(a) shows the infrared spectrum of pristine MWCNTs. The spectrum does not show any sharp infrared peaks, it means it may not contain any functional groups. Similarly Fig. 2(b)shows the infrared spectrum of oxidized MWCNTs. If we compare this spectrum to that of IR spectrum of pristine MWCNTs, many changes can be seen. New peaks are arises. Integrity of hexagonal structure on MWCNTs was confirmed by appearance of peak at ~1600 cm^{-1} elucidating existence of carbon double bonding (C=C). Appearance of peak at ~1750 cm^{-1} assigns carbonyl (C=O) stretching vibration of carboxyl groups, indicating the expansion of carboxylation on the surface of oxidized MWCNTs [16].

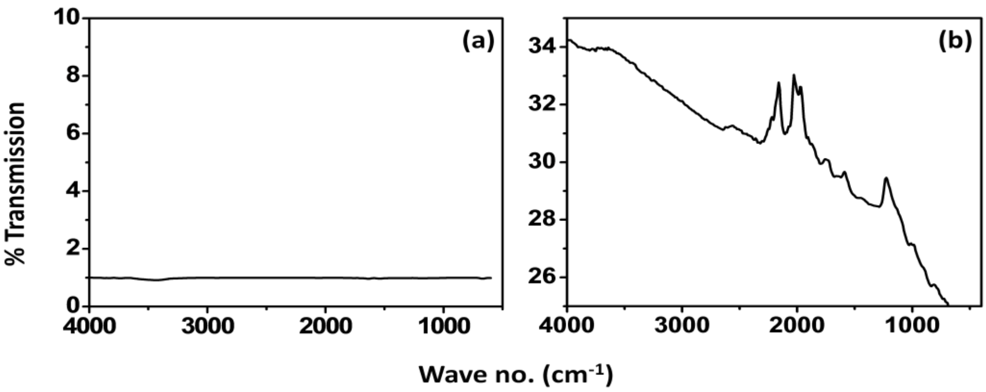

Fig. 2. Infrared spectrum (a) pristine MWCNTs (b) Oxidized MWCNTs.

4.2 Scanning Electron Microscopy (SEM)/ Energy Dispersive Spectroscopy (EDS)

SEM is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. Here, Fig.3 shows the SEM images of the Ni-decorated oxidized MWCNTs film deposited on the stainless steel substrates.

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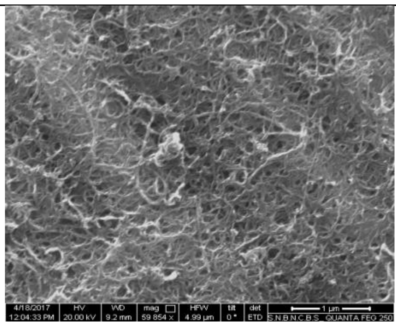

Fig. 3. Scanning Electron Microscopic image Ni decorated MWCNTs on stainless-steel substrate

The images indicate the uniform deposition and high packing density of samples on the substrates. This observation is in accordance with the deposition characteristics reported by Thomas et al. [17] who performed CNT film deposition by EPD on stainless steel substrates.

Energy dispersive spectroscopy is used for the elemental analysis or chemical characterization of a sample. Its characterization capability is due to its fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum. The presence of expected metallic nickel on electrophoretic deposited Ni decorated MWCNTs on substrate was confirmed by EDS.

4.3 I-V Curve Analysis

Here, I-V curve characterization of Ni-decorated MWCNTs at different voltages were analyzed via electrolysis using 0.1M NaOH as electrolyte. Fig. 4 shows the I-V curve of Ni decorated MWCNTs deposited on steel plate by EPD process.

Here, our experiment found that over potential is 2.6 V and 2.5V obtained from EPD of Ni-decorated MWCNTs at initial and 3 hrs observation respectively. The slope of curve for the 3 hours observation is slightly lower than initial curve.

The hydrogen gas was evolved from cathode which was made from Ni- decorated MWCNTs deposited by electrophoretic deposition technique. Some limitations were arise during the process. During electrolysis process, when high concentration of electrolyte was use, the deposited MWCNTs were slowly detached from substrates. So, low concentration of electrolyte was used. In our work, MWCNTs was not strongly attached to the substrate. The slight decrease of slope may be due to slight detached of Ni-MWCNT from the substrate. If this problem may overcome by any method, the rate of hydrogen gas production may be improved with decrease of over potential.

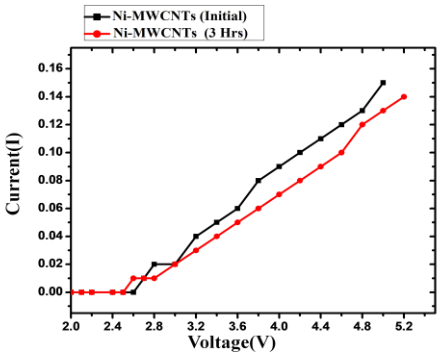

Fig. 4. Comparison of I-V curve of electrophoretic deposited Ni-decorated MWCNTs.

5. Conclusions

The electrophoretic deposition process has gained considerable attention for fabrication of advanced materials. This is simple and cost effective method for deposition. The nickel decorated MWCNT was deposited on steel substrate by EPD process. The nickel nanoparticles were decorated on the surface of oxidized MWCNT by wet chemical route by using ethylene glycol as reducing agent. Oxidation of MWCNTs was conducted by using conc. nitric acid. Presence of oxygen functional group was detected by FTIR spectroscopy. The presence of expected nickel metal on the surface of MWCNT was shown by Energy Dispersive Spectroscopy. The electrophoretic deposition was carried out on steel substrate by EPD process. The SEM revealed the uniformly deposition of Ni-MWCNT on steel substrate.

The electrophoretic deposited Ni-decorated MWCNTs may be applied for the production of hydrogen gas via alkaline electrolysis using NaOH as electrolyte. Thealkaline water electrolysisis easiest and simple method to produce hydrogen gas. Our study showed that Nickel decorated MWCNTs may be used for the production of hydrogen gas.

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7. References

[1]. X. Wang, L. Quniqing, X. Jing, J. Zhong, W. Jinyong, L. Yan, J. Kaili and F. Shoushan, Fabrication of ultralong and electrically uniform single-walled carbon nanotubes on clean substrates,*Nano Letters, 9,* 2009**,** 3137-3141.

[2]. S. Iijima, Helical microtubes of graphitic carbon, *Nature*, *354,* 1991, 56-58.

[3]. R. Rastogi, R. Kaushal, S.K. Tripathi, A.L. Sharma, I. Kaur and L. M. Bharadwaj, Comparative study of carbon nanotube dispersion using surfactants, *Journal of Colloid Interface Science*, *328*, 2008, 421-428.

[4]. B.J.C. Thomas and A.R. Boccaccini, MWCNTs coating using EPD, *Journal of American Ceramic Society, 88[4]*, 2005, 980-982.

[5]. A .R. Boccaccini, P. Karapappas, J. M. Marijuan and C. Kaya, "TiO_2 coating on silicon carbide and carbon fibre substrates by electrophoretic dispersion, *Journal of Material Science, 393[3],* 2004, 851-857.

[6]. O. Van der Biest and L. J. Vandeperre, Electrophoretic deposition of materials, *Annual review of Material Science,29*, 1999, 327–352.

[7]. P. Sarkar and PS. Nicholson, Electrophoretic deposition (EPD): mechanisms, kinetics, and application to ceramics, *Journal of the American Ceramic Society*, *79[8],* 1996, 1987–2002.

[8]. R. Solmaz and G. Kardas, Electrochemical deposition and characterization of NiFe coatings as electrocatalytic materials for alkaline water electrolysis, *Electrochimica Acta*, *54*, 2009,3726-3734.

[9]. G. Passas and CW. Dunnill, Water splitting test cell for renewable energy storage as hydrogen gas, *Fundamentals of Renewable Energy and Applications*, *Volume 5, Issue 5* • 2015, 1000188.

[10]. P. C. Ma , N. A. Siddiqui, G. Marom and J. K. Kim, Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites, *Compos. A,41*, 2010, 1345–1367.

[11]. L. Bokobza and J. Zhang, Raman spectroscopic characterization of multiwalled carbon nano composites, *Express Polymer Letters*, *6[7],* 2012, 601-608.

[12]. C. Bittencourt, A. Felten, J. Ghijsen, J. J Pireaux, W. Drube, R. Erni and G. V. Tendeloo, *Decorating carbon nanotubes with nickel nanoparticles*, *Chemical Physics Letters*, *436(4),* 2007, 368–372.

[13]. A. Priscilla, Selembo, D. Mettew, Merrill and B. E. Logan, Hydrogen production with nickel powder cathode catalysts in microbial electrolysis cells, *International Journal of Hydrogen Energy, 35(2),* 2010, 428-437.

[14]. S. Abdel Aal, A. S. Shalabi and K. A. Soliman, High capacity hydrogen storage in Ni-decorated carbon nanocone, *Journal of Quantum Information Science, 5,* 2015, 134-149.

[15]. A. Fraczek-Szczypta, E. Dlugon, A. Weselucha-Birczynska, M. Nocun and M. Blazewicz, Multi walled carbon nanotubes deposited on metal substrate using EPD technique. A spectroscopic study, *Journal of Molecular Structure, 1040,* 2013, 238-245.

[16]. R. Yudianti, H. Onggo, Sudirman, Y. Saito, T. Iwata and J. Azuma, Analysis of functional group sited on multi-wall carbon nanotube surface, *The Open Materials Science Journal, 5,* 2011, 242-247.

[17]. B. J. C. Thomas, A. R. Boccaccini and M. S. P. Shaffer, Multi-Walled carbon nanotube coatings using electrophoretic deposition (EPD), *Journal of American Ceramic Society, 88 [4],* 2005, 980–982.