

Carbon Based Nanostructures For Energy Storage

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Abstract

Materials can be made from several types of elements, either in the pure elemental form or in the form of compounds and composites. Generally, bulk materials can be classified broadly as metals, semiconductors, and insulators. And when any of these materials is produced in the nanometer scale, each displays shape-/size-dependent properties. These new properties have the potential to provide enormous opportunities for both scientists and engineers to create many novel applications that are normally not possible with conventional bulk materials. Many of the nanometer-scale properties (e.g., size, shape, surface structure, and chemical composition) have only been deciphered since the advent of advanced microscopic techniques, which has enabled researchers to precisely measure and directly visualize materials at the atomic scale in real time, something impossible just a few decades ago. And, even more impressive is the ability of these characterization techniques to give us a glimpse of materials and processes in their own localized micro-/nanoscopic environment. The nanometer-scale materials had different and remarkable properties originated with the discovery of buckminster- fullerene (C₆₀ or buckyball) in 1985. Subsequent studies ultimately led to the discovery of several other forms of exotic carbon structures, such as carbon nanotubes (CNTs; both single wall and multiwall), intercalated CNTs, carbon nanohorns, and recently graphene. These discoveries spurred researchers worldwide to actively investigate other nanometer- scale materials, especially those with inherently novel properties that could be proprietarily secured via trademarks and patents. Today, the range of elements and compounds successfully synthesized in nanometer-scale forms, characterized, and even deployed as commercial products include Metals, Metal oxides, Polymers, Semiconductors, Carbon compounds. The paper presents the processing and properties of different types of nanomaterials. In addition, the methods for the synthesis of different types of 1 D carbon nanotubes (CNTs) by the catalytic chemical vapour deposition (CCVD) technique by the pyrolysis of suitable hydrocarbons over selective alloy hydride catalysts and the processing of 2D.

Keywords: Preparation, Processing, Properties, methods for the synthesis, Experimental techniques.

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1. INTRODUCTION

Carbon nano tubes (CNTs) are currently the focus of intense research world wise because of their unique properties that could impact various areas of science and technology. Recent experimental studies have shown that CNTs have mechanical strength suggesting their potential for advanced composites. The remarkable electronic properties offer them great potential for novel applications including various nano-devices. Because of their small diameter involving only a small number of carbon atoms and due to their large aspect ratio, CNTs are classified as one-dimensional (1D) carbon systems and most of the theoretical studies on CNTs emphasize their 1D properties. The most interesting of these theoretical developments was the prediction that SWNTs could be either semiconducting or metallic depending on their geometrical characteristics. Extensive effort has been taken to study the structural, electrical, mechanical and chemical properties of CNTs in order to explore the potential applications of these novel materials. The properties and applications of CNTs have been extensively reviewed by several authors. The recent developments in this field have generated great excitement in the area of nano scale science and technology. ^[1]

CNTs can be used individually or as assembly for its various applications such as to build nano-electronic devices such as field effect transistors and rectifying electrodes. Bundles of nanotubes have been used for field emission based flat panel displays and other applications such as CNT based sensors and filters. Individual nanotubes have been used as tips for scanning probe microscopy. Bulk quantities of CNTs have also been used in other applications such as hydrogen storage media and composite materials with improved mechanical properties. ^[2]

For realizing the possible applications of the CNTs, controlled and optimized growth of nanotubes is very significant. The nano-electronic applications require controlled and selective growth of CNTs on substrates. ^[3]

Most of applications demand high quality nanotubes in high yield. Even though lots of work has been carried out in recent years towards overcoming these issues, growth methods for large scale production of CNTs that are simple, efficient and inexpensive is still a major challenge. In recent years, chemical vapour deposition (CVD) method has been shown to be promising for producing nanotubes with different morphologies in large quantities which is essential for various applications. ^[4]

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Graphene is a single sheet of graphitic carbon wherein the carbon atoms are tightly arranged in a 2D honeycomb like lattice. Graphene remained a theoretical construct for more than 70 years until its recent extraction in minute quantities by micromechanical cleavage. Whereas an efficient method to produce large quantities of single layer grapheme still eludes the scientific community, a variety of methods for preparing (few) layered grapheme sheets do exist: thermal exfoliation of graphite oxide, conversion from nanodiamond etc. Graphene sheets have excellent properties which make them suitable for a variety of applications. Intrinsic grapheme is a semi-metal or a zero gap semiconductor. It has a linear energy dispersion relation resulting in zero charge carrier density (Dirac fermions). Exceptionally high electron mobility at room temperatures, with values in excess of $15000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ has been reported. However, with the increase in the number of layers these properties are expected to evolve and finally match those of bulk graphite. Interestingly, though not unexpected, few layered grapheme is expected to retain many of the properties of single layer grapheme and are hence suitable for a host of applications: FETs, transparent conductors, integrated circuits, ultracapacitors etc. Graphene with its extremely large surface area is also expected to be excellent materials for gas sensing applications. It is expected that with the introduction of defects and suitable dopants, graphene sheets can be engineered to detect suitable gases. [5]

In this paper, we present the progress made in the synthesis of different types of nanomaterials and 1 D CNs by CCVD and 2 D graphene by exfoliation of graphite oxide. Synthesis of MWNT, SWNT and metal/alloy encapsulated MWNT by pyrolysis of selective hydrocarbon over suitable alloy hydride catalysts, prepared by hydrogen decrepitation technique, will be focussed. The proposed growth mechanism of metal/alloy encapsulated MWNT produced by this technique and the various characterization methods employed are also discussed. Further, some of the applications of these CNTs with an emphasis on energy-related applications such as catalyst support material in hydrogen and alcohol based fuel cells (PEMFC, DMFC, DEFC), hydrogen sensors and hydrogen storage media are discussed in detail. [6]

2.Synthesis of single walled carbon nanotubes, multi walled carbon nanotubes and magnetic metal-filled multi walled carbon nanotube by CCVD:

A novel, cost effective, easy and single step process for the synthesis of SWNT, MWNT and metal-filled MWNT, in large quantities using Mischmetal (Bharat Rare Earths Metals, India; composition: Ce 50%, La 35%, Pr 8%, Nd 5%, Fe 0.5% and other rare earth elements 1.5%) based AB_3 ($\text{B}=\text{Ni}/\text{Fe}/\text{Co}$) alloy hydride catalyst, obtained through hydrogen decrepitation technique. Catalytic chemical vapour deposition (CCVD) technique using a single-stage furnace facility has been used to grow these nanostructures in the temperature range 900°C to 1050°C . The carbon deposit obtained at 900°C shows the presence of MWNT. SEM image of the as grown MWNT synthesized over Mm based AB_3 alloy hydride catalyst with Ni at the B site at 900°C shows the presence of catalytic particles at the tips of the MWNTs. The selective EDAX pattern from the MWNT tips show the

presence of Ni which is responsible for the nucleation of CNs. These catalytic impurities can be removed by refluxing with con nitric acid for approximately 24hr. SEM, TEM and HRTEM images of purified MWNT show an inner diameter of about 15 nm and outer diameter of around 60 nm.

Raman spectrum obtained from a Renishaw aRaman spectrometer using 514.5 nm excitation of the MWNT and SWNT shows typical tangential modes corresponding to the Raman allowed optical mode E_{2g} of two-dimensional graphite, centered around 1580cm^{-1} (G-band) observed for all the samples. In addition, a peak centered at around 1350cm^{-1} (D-band) is mainly due to defects and carbonaceous particles present in the sample. The intensity of D- band gives the degree of disorder present along the tube. [7]

3.Performance of PEMFC using Pt/MWNT-Pt/C composites as electrocatalysts for oxygen reduction reaction in PEMFC:

Purified MWNT were ultrasonicated in 10 ml of acetone for 1 hr and then $0.075\text{ M H}_2\text{PtCl}_6$ was added slowly during stirring. After 12 hr, the mixture was reduced by adding reducing solution containing 0.1 M NaBH_4 and 1 M NaOH . After completion of reaction, the solution was washed with de-ionized water, filtered and dried by vacuum filtration using a filter. The recovered Pt loaded MWNT were dried at 80°C for 3 hr. The crystallinity of the samples was obtained by X-ray powder diffraction (XRD) analysis, performed with a monochromatic $\text{Cu-K}\alpha$ radiation. Morphological characteristics of CNTs were obtained using scanning electron microscopy (SEM) and Transmission electron microscopy (TEM).

The membrane electrode assembly (MEA) was obtained by sandwiching a pre-treated Nafion 1135 (Nafion R) membrane between the anode and the cathode. Both the anode and cathode layers consisted of a backing layer, a gas diffusion layer and a catalyst layer. To prepare the catalyst layer, the required amount of catalyst was suspended in de-ionized water and ultrasonicated by adding 5wt% Nafion solution. The suspension was spread uniformly over a carbon fabric (SGL Carbon). The electrodes were of 11.56 cm^2 area. The electrodes were sandwiched by hot pressing at 130°C and 70 bar for 2 min. The anode was a $3.4 \times 3.4\text{ cm}^2$ 20% Pt/C electrode, with a platinum loading of 0.25 mg cm^{-2} . The cathode was prepared from a suspension containing mixture of Pt/MWNT (Pt content of 20wt %) and Pt/C (Pt content of 20 wt%), with a platinum loading of 0.5 mg cm^{-2} . A single PEMFC was assembled using the MEA, two graphite plates with gas channels machined with a serpentine geometry, two Teflon gaskets and two aluminium end plates. The performance of the PEMFC was studied in an indigenously fabricated Fuel Cell test station, using a dc electronic load box. Since hydration of the electrolyte membrane is important for attaining maximum performance of the PEMFC, reactant gases were humidified with water. [8]

4.SEM, TEM HRTEM images of Pt loaded MWNT:

A TEM image of the Pt/MWNT shows more or less uniform distribution of noble metal particles of size of about 3-5 nm on the CNTs. The HRTEM image of Pt/MWNT clearly indicates lattice planes of Pt particles indicating crystalline nature of catalytic Pt. The energy dispersive

analysis (EDAX) shows that the amount of Pt loaded on the carbon nanotube support with reference to carbon can be evaluated qualitatively as 20%. The polarization curves were obtained from the single cell PEMFC using the same type of anode. Prior to polarization studies, the electrodes were activated between open-circuit potential and high current densities. The activation cycle is necessary to activate the catalyst for the oxygen reduction reaction. The performance of Pt/MWNT electrocatalysts, prepared using pre-treated MWNT grown over Mm based AB3 alloy hydride catalysts, mixed with varying amounts of commercial Pt/C as cathode catalyst in PEMFC, under an operating pressure of 1 bar. In the low current density region, the voltage drop in the potential-current curve, generally known as activation polarization, reflects the sluggish kinetics intrinsic to the oxygen reduction reaction at the cathode surface. The voltage drop in the mid to high current density range, or ohmic polarization, arises from limitations in proton transport through the electrolyte membrane from anode to cathode and/or limitations in electron flow in the electrode materials. Better performance of PEMFC was observed for cathode catalyst with Pt/MWNT content compared to those containing commercial Pt/C which could be attributed to higher catalytic activity of smaller Pt particles with uniform sizes decorated on the MWNT. The higher performance of the Pt/MWNT electrodes compared to the Pt/C electrodes could be ascribed to the networks and interiors of CNTs consisting of spaces for gas diffusion and high electric conductivity of MWNT. Pt/Ru/multiwalled carbon nanotubes as electro catalyst for Direct methanol fuel cell.

5. Pt-Ru/multiwalled carbon nanotubes as electrocatalysts for Direct Methanol Fuel Cell:

Purified MWNT were ultrasonicated in 10 ml of the acetone for 1 h and then 0.075 M H_2PtCl_6 and 0.15 M $RuCl_2$ solutions were added slowly during stirring. After 12 h the mixture was reduced by adding reducing solution containing 0.1 M $NaBH_4$ and 1M $NaOH$. After completion of reaction the solution was washed with de-ionised water, filtered and dried by vacuum filtration. The recovered Pt-Ru loaded MWNT were dried at 800°C for 3h. Here in DMFC, membrane electrode assembly (MEA) was obtained by sandwiching a pre-treated Nafion 1110 membrane between the anode and cathode. The anode was Pt-Ru/MWNT, with a loading of 2.5 mg cm^{-2} . The cathode was prepared from a suspension containing mixture of Pt/MWNT and 20% Pt/C, with a platinum loading of 5 mg cm^{-2} . Humidified oxygen was passed to the cathode at the flow rate of 180 sccm and 1M methanol at the anode through the serpentine channels of DMFC.

6. Conclusion:

Today, the entire world faces an energy crisis such as never seen before, and many nations have to rely exclusively on costly imported fossil fuels to generate electricity to power their economy and provide energy for the population. Even in advanced economies, fossil fuels are increasingly becoming expensive and have a polluting cost associated with their continued use. Nanotechnology has shown many glimpses of instances for manipulating nanomaterial to create new avenues for sustainable clean energy and potential solutions for the future.

The nanocarbons created in Laboratory can be used to coat a simple Cu metal foil and the temperature profile plotted versus time when this carbon-coated foil is placed in direct sunlight. The levels of coatings and nature of the nanocarbons contributing to the profile can be investigated. Carbon bucky paper can be readily made from either a commercial source of carbon nanotubes (CNTs) or using graphene-based materials. These can then be characterized with the nanotools described previously and made into electrode substrates for the microbes (either on its own or also doped with metallic NPs). Then, the efficiency of these cells can be evaluated. Fuel cells can be an alternative source of power, and one active area of research and development is in microbial fuel cells (MFCs). In this type of cell, microbes are utilized to generate hydrogen that can be used as a source of fuel. Carbon buckypaper can be readily made from either a commercial source of carbon nanotubes (CNTs) or using graphene-based materials. These can then be characterized with the nano tools described previously and made into electrode substrates for the microbes (either on its own or also doped with metallic NPs). Then, the efficiency of these cells can be evaluated.

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