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Nanotechnology and Nanomaterials for New and Sustainable Energy Engineering

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Role of nanotechnology and nanomaterials for utilization, storage and generation of hydrogen energy, generation of environment friendly thermoelectric power, generation of geothermal energy and photovoltaic or solar energy has been explored. Graphene nanosheet has emerged as a promising material for Platinum catalyst support of fuel cell to enhance electrochemically active surface area and power generation. Graphene and graphene based nanocomposites namely graphene-Polyaniline (PANI) are explored as promising alternatives for hydrogen storage. Inorganic-organic nanocomposite electrolyte membranes comprising of nanosize inorganic building block offers higher proton conductivity, ion exchange capacity and enhanced power generation when applied in a fuel cell. Nanostructured thermoelectric material enhances the power factor and figure of merit. Inorganic (bismuth telluride) –organic (conducting polymer) nanocomposites are explored as a new class of thermoelectric material.

Keywords: Energy engineering, sustainable, Nanotechnology, Nanomaterials, Hybrid, Hydrogen energy, Thermoelectric, Geothermal, Nanocatalysts, Nanostructures, Photoelectric and photovoltaic, Conducting polymers.

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1. INTRODUCTION

Nanotechnology, nanomaterials and sustainable energy engineering may arguably be some of the most important topics to influence human life in the near foreseeable future. With the reducing reserves of conventional energy sources like oil, natural gas and coal, it becomes imperative to augment research efforts on new and sustainable energy sources. It is extremely interesting to note that all the new age energy sources like hydrogen energy, thermoelectric energy, geothermal energy, photovoltaic and solar energy etc needs the help of nanotechnology and nanomaterials to augment the efficient storage, generation, utilization and perhaps even transmission in the future. Nanotechnology and nanomaterials add substantially the promise and potential of the new and sustainable energy utilization in commercial scale.

2. HYDROGEN ENERGY

2.1 Nanotechnology and Nanomaterials for Hydrogen Utilization

In the wake of the emerging market potential for fuel cells and green energy generation using hydrogen as raw material, it becomes imperative to research upon the development of nanomaterials to improve its real-life performance. The proton exchange membrane fuel cell (PEMFC) and the phosphoric acid fuel cell (PAFC) are particularly in the focus of interest as some of the most promising power generator for a wide range of applications in transportation and in portable electronics. These fuel cells convert the chemical energy of the fuel and oxidant into electrical energy. The major material components are the conductive electrolyte membrane and the catalysts/electrodes.

2.1.1 Nanotechnology and Nanomaterials for Fuel Cell Electrodes

In order to enhance catalytic activity and to reduce the usage of Pt-based catalysts, one strategy is to explore novel carbon materials as catalyst supports and to effectively disperse Pt-based particles on these supports. During the past several years, a few research groups have investigated graphene, one type of novel carbon nanostructures, as a catalyst support and have demonstrated that graphene can improve the electrocatalytic activity of Pt nanoparticles more effectively for oxidation than Vulcan XC-72R carbon black [1, 2, 3] in PEM Fuel Cell.

Graphene is an exhilarating material; It is a 2D single layer of carbon atoms with the hexagonal packed structure. The carbon bonds are sp^2 hybridized, where the in-plane σ C-C bond is one of the strongest bonds in materials and the out-of-plane π bond, which contributes to a delocalized network of electrons, is responsible for the electron conduction of graphene and provides the weak interaction among graphene layers or between graphene and substrate. It has a large theoretical specific surface area (2630 $m^2 g^{-1}$), high intrinsic mobility (200 000 cm 2 $v^{-1} s^{-1}$), high Young's modulus (~1.0 TPa). Its high optical transmittance (~ 97.7%) and good electrical conductivity make it attractive for applications of transparent conductive electrodes.

To improve the energy efficiency and performance of fuel cell system, graphene as a catalyst support material is synthesized using a new method (combined form of Modified Hummers Method and Improved method). Graphene is characterized using TEM, Raman Spectroscopy, FTIR, XRD. TEM images. Fig. 1 shows single and multilayer layer graphene sheets. Figure 2 shows the Raman Spectroscopy of graphene sheet. In the Raman spectrum the G band is broadened

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and shifted upward to 1595 cm -1. At the same time, the intensity of the D band at 1350 cm-1 increases substantially. These phenomena could be attributed to the significant decrease of the size of the in-plane sp2 domains due to oxidation and partially ordered graphite crystal structure of graphene nanosheets.

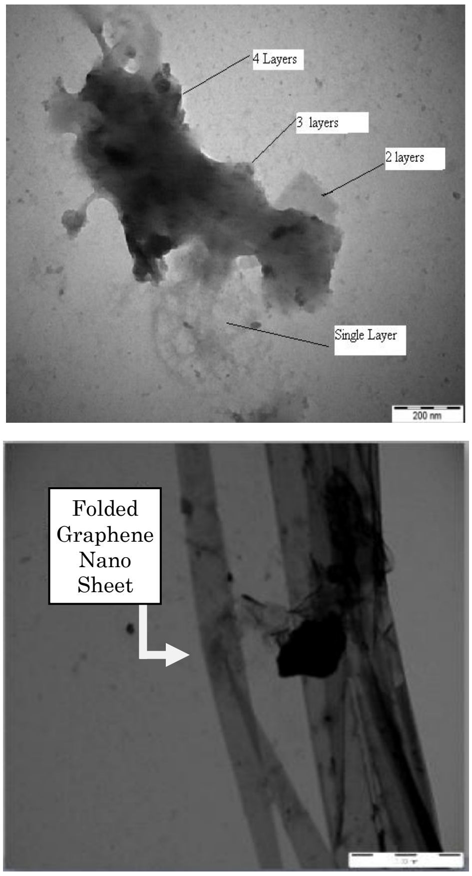

Fig. 1 – TEM analysis of Graphene

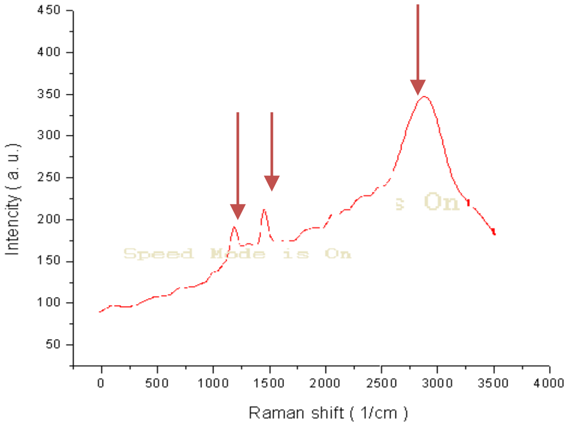

Fig. 2 – Raman Spectroscopy of Graphene

Dispersion of the electrocatalyst on graphene has been found to be useful for achieving relatively better performance in fuel cells. Almost 80% increase in electrochemical surface area (ECSA) can be achieved by using graphene as a catalyst support [2]. It is reported in literature that the partially reduced GO-Pt based fuel cell delivered 60% enhanced maximum power compared to that for an unsupported Pt based fuel cell [2].

2.1.2 Nano-enhancement of Electrolyte Membrane Performance

The performance of PEMFC is dependent on the proton conductivity, ion exchange capacity and water uptake of the electrolyte membrane. Inorganic-organic hybrid nanocomposite membranes generated substantial research interest due to their potential of having a wide range of physical, chemical, thermal and mechanical properties. Inorganic-organic nanocomposite membranes comprising of nanosize inorganic phase/building block often demonstrate interesting properties due to nano scale of constituent phases, high interfacial area and synergetic properties. The structural and physiochemical properties and hence the performance of such composite membranes depends on their composition, size of the inorganic particle, interfacial interactions etc.

Hybridization of sub-micro and nano particles of inorganic gel with functional polymer (example Sulfonated poly ether ether ketone (SPEEK)) for fuel cell membrane electrolyte enhances its proton conductivity, water uptake and ion exchange capacity. Fig. 3 shows almost 50% enhancement of value of proton conductivity of phosphosilicate gel-SPEEK electrolyte membrane by varying the particle size of inorganic gel from submicrometer to nanometer range.

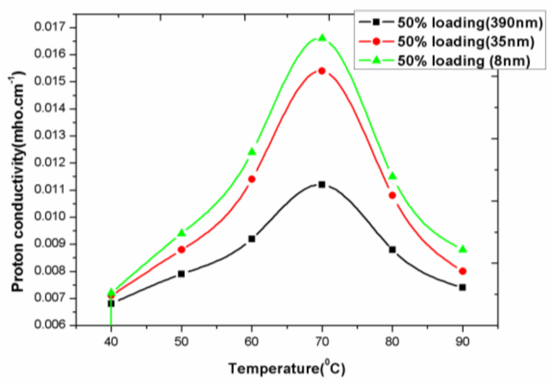

Fig. 3 – Effect of particle size of Phosphosilicate gel on the proton conductivity of the composite membrane

Nano-structuring improves proton transport behavior even at lower humidity conditions, allows higher loading of inorganic gel and improves the current vs voltage and power vs current characteristics. Almost 50% enhancement in power generation is achieved by replacing the composite hybrid membrane with coarse sub-micrometer size phosphosilicate particles by a nano composite membrane comprising of less than 10 nm particles (Fig. 4). Percent enhancement varies exponentially with reduction in the size of inorganic building block [4].

2.2 Nanotechnology and Nanomaterials for Hydrogen Storage

A two-dimensional, single-layer sheet of sp2 hybridized carbon atoms namely Graphene nanosheet or reduced Graphene Oxide and its hybridized variants have attracted tremendous attention and research interest in different fields of energy engineering among others. Interest in Graphene's wonderful physical properties, chemical tunability, and potential for applications in a variety of high impact energy applications

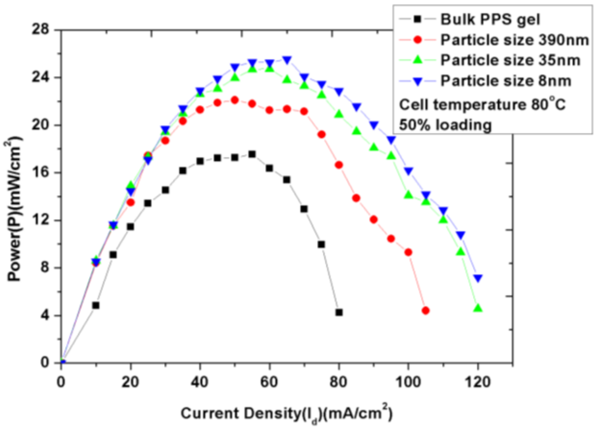

Fig. 4 – Effect of phosphosilicate gel particle size on Power density versus Current density for the fuel cell

have promising potentials in the future. The synthesis, characterization of Reduced Graphene Oxide and Graphene nanosheet as well as Graphene derived Nanocomposites has already been achieved using graphite oxidation, ultrasonic exfoliation and chemical reduction and other chemical approaches.

Graphene-based nanomaterials have recently shown fascinating applications as electrochemical sensors and in Hydrogen storage [5,6]. Owing to the surprising electronic transport property and high electrocatalytic activity of graphene, the electrochemical reactions of analyte are greatly promoted on graphene film, resulting in enhanced voltammetric response [7,8]. Moreover, the electrochemical properties of graphene can be effectively modified by integration with other functional nanomaterials such as catalyst nanoparticles to produce versatile electrochemical performances [9-13]. Nanostructured Graphene have received continuous interest as potential hydrogen storage media. Out of the variety of composites that need to be researched upon, attempts were made with various types of graphene_PANI composites and they showed enhanced electrochemical characteristics as electrode materials for energy storage devices.

The Transmission Electrone Microscope (TEM) images of Graphene-PANI is given in the following figure. FTIR is performed for graphene (G), graphene oxide (GO) and G-PANI. The results obtained are as given in Fig. 6. The figure shows the FTIR image of GO and graphene sheet. The oxygen-containing functional groups of graphite oxide were indicated by the bands at 1730, 1382, 1240 and 1062 cm^{-1}, which correspond to C O stretching vibrations, C–O–H deformation peak, C–OH stretching peak and C–O stretching peak, respectively. Oxygen containing functional groups were almost removed in the process of reduction with hydrazine hydrate, and thus the graphite oxide was transformed into graphene sheet in the syntheses.

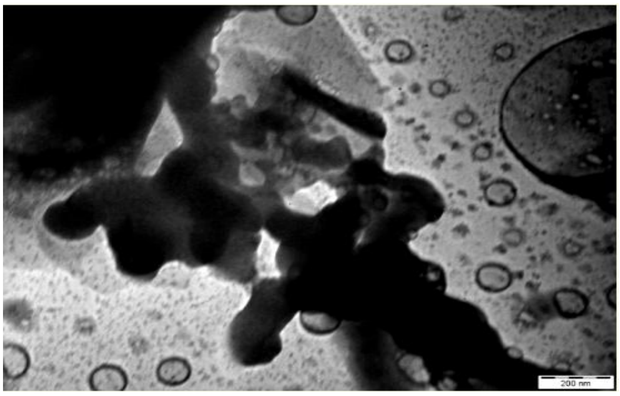

Fig. 5 – TEM images of G-PANI (200 nm)

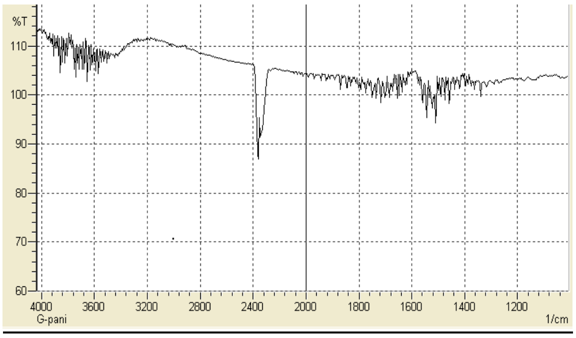

Fig. 6 – FTIR results for Graphene-PANI nanocomposites

For the FTIR spectrum of the Gr–PANI Nano composite, the C–N and C-C stretching of the quinonoid and benzenoid units appeared at 1559 cm^{-1} and 1478 cm^{-1}, respectively. The band at 1292 cm−1 is assigned to the C–N stretching of the benzenoid unit. The broad band at 3440 cm^{-1} can be assigned to the overlapping of the strong adsorption of the N–H stretching vibrations of PANI and OH groups of graphene.

The amount of hydrogen storage is characterized by the analysis of TEM, SEM, XRD and TGA results. The results for Graphene-PANI nanocomposites will be discussed in the present presentation.

Other hydrogen storage nanomaterials like boron derivatives, amine boranes, carbon nanotubes etc. have been cited in the present overview.

2.3 Nanotechnology and Nanomaterials for Hydrogen Generation

During the development of dehydrogenation of hydrogen storage complexes like dimethylamine-borane, nanoparticle catalysts like ruthenium (III) chloride to the hydrogen storing complexes causes substantial enhancement of hydrogen production. Nanocatalysts provide higher proportion of surface active atoms resulting in enhanced catalytic activity leading to faster hydrogen generation.

Another recently developed nanomaterial is molybdenum disulphide nanoparticles hybridized on graphene or reduced graphene oxide (RGO). Flexible graphene oxide sheets act as an ideal substrate for molybdenum disulphide nanoparticles. The generated molybdenum disulphide on reduced graphene oxide hybrid has a very high electrocatalytic activity for the hydrogen evolution reaction. The very high value of the experimental Tafel slope shows significant increase of the rate of electrochemical reaction.

Photocatalytic hydrogen evolution from sea water or salt water using nanocatalysts like $ZnS_nO_x(OH)_yZnO$ impregnated with electron donor sulfide ion (Na_2S–Na_2SO_3) etc holds considerable promise for futuristic generation of hydrogen.

3. THERMOELECTRIC ENERGY

Thermoelectric materials have recently attracted research efforts due to their unique properties of mutual conversion between temperature gradient and electricity. The advantages of using thermoelectric materials arise due to their reliability, miniaturized modules and environment friendly nature. The efficiency of thermoelectric material is quantitatively related to figure of merit $Z = S c/k = P/k$ where S is the thermoelectric power, c is the electrical conductivity, k is the thermal conductivity and P is the power factor. Interestingly, nanostructuring of material enhances both S and P due to quantum confinement. Size effect leads to carrier confinement. Selective scattering and interface scattering reduce the thermal conductivity more than the electrical conductivity and thus enhance the figure of merit. Bismuth telluride is the best known thermoelectric material for room temperature applications.

With the advent of conducting polymers, research on hybridization gained significance in the field of thermoelectricity. Consequently, a wide number of conducting polymers, such as, polyacetylene, poly (p- phenylene), polypyrrole, polyaniline and many more, has been studied. Conducting polymers are potential thermoelectric materials due to their low thermal conductivity compared to that of inorganic materials.

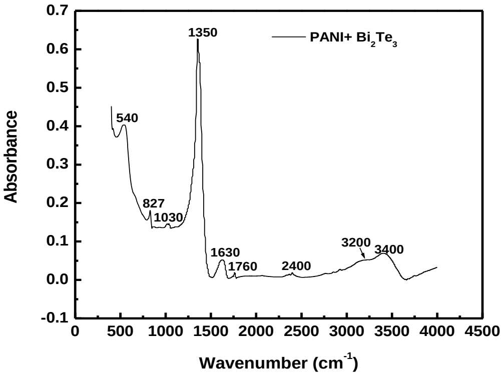

Fig. 7 – FTIR spectra of PANI/ Bi_2Te_3 composite

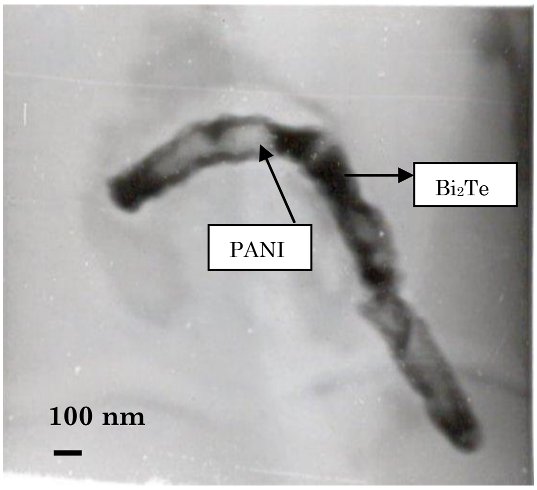

Fig. 8 – TEM micrographs of PANI/Bi_2Te_3 composite

The transport properties of the conducting polymers are greatly influenced by the process of doping with different materials. Polyaniline (PANI) is a very attracting polymer for its diversifying structure, facile synthesis, environmental stability and redox reversibility, involving the exchange of protons and electrons. It has attracted much attention due to its possible applications in electrochromic display, schottky diodes, sensors, optoelectronics devices and electromagnetic shielding. For the improvement and enhancement of the properties of PANI, different protonic acids have been used as dopants.

Nanoenhancement of properties of PANI, doped with inorganic bismuth nitrate with different concentration (weight ratio) have been reported in literature and has promising potential as futuristic material in thermoelectric research [14-16].

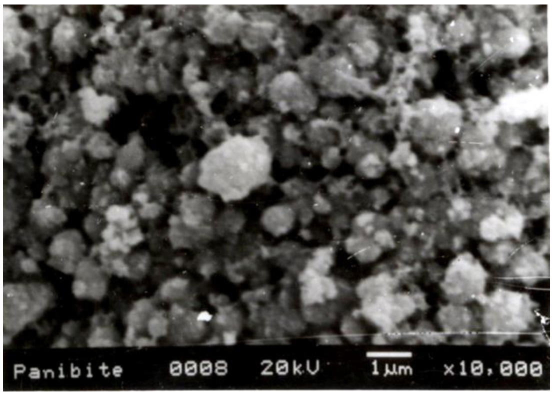

Fig. 9 – SEM of PANI/Bi_2Te_3 composite

4. OTHER NEW ENERGY TECHNOLOGIES

4.1 Nanotechnology and Nanomaterials for Geothermal Energy

The energy contained in the core of the earth provides a source of inexhaustible energy and has the potential to meet all the energy demands of the future. However, the major problems encountered in the field of geothermal energy utilization is the requirement of deep borings often causing tremors or earthquakes. Recent research have found that nanostructures of certain materials can encapsulate or absorb substantially higher orders of energy as compared to the normal thermal fluids. This observation opens up a range of future research prospects of using less deep borings and nanomaterials to utilize geothermal energy.

4.2 Nanotechnology and Nanomaterials for Solar Energy and Photovoltaics

Photovoltaics involve the engineering expertise to generate electricity from light and recently it is developing into an important industrial product of the future. Wafer based crystalline Si cells are presently used. The high capital costs and operational costs limit the use of this technology today. The low efficiency of solar cells and the expensive capital investments for large-scale electricity generation makes it a less popular option today. However, the cost of these cells is likely decrease in the future by using thinner wafers and nanocomposite devices with higher conversion efficiency.

5. CONCLUSIONS

The current research achievements in several new and sustainable energy engineering directions have been explored in this presentation. It was interesting to observe that nanotechnology and nanomaterials largely augment and improve the promise and potential of these emerging new horizons of energy research for application in commercial scale in the future. Several new hybridized nanomaterials and nanotechnologies have been cited in this presentation.

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