Abstract

Method for the Large Scale Manufacturing of Graphene Polyhedral Structures

The present invention disclosed a method for manufacturing Graphene polyhedral structures by using chemical vapor deposition (CVD) of methane as precursor gas and a mixture of alkaline earth metal and transition metal as catalyst. The Graphene nanosheets formed in the present invention have hollow, porous, multi-wall carbon nanospheres or polyhedral structures with a narrow size distribution and an average particle size of approximately 80 nm and an average aspect ratio close to 7:5

I claim:

1. A process to provide a large scale substrate free manufacturing process for the cost effective production and efficient industrial scale method of high purity Graphene polyhedral structures by utilizing chemical vapour disposition.

2. The process as claimed in claim 1 wherein the said process utilizes methane as a carbon source.

3. The process as claimed in claims 1 to 2, wherein a mixture of alkaline earth metal and transition metal as catalyst.

4. The process as claimed in claim 3 wherein the catalysts comprise of Fe:Co:Mg. and the preferred ratio of metals is 1:1:38.

5. The process as claimed in claims 1 to 4 herein the required amount of catalysts are loaded in Chemical Vapor Deposition (CVD) reactor.

6. The process as claimed in claim 5 wherein chamber of CVD first evacuated with vacuum and then purged with argon gas.

7. The process as claimed in claims 1 to 6 wherein methane gas is purged into the reactor vessel along with argon whenever the CVD temperature reached a desired temeperature,

8. The process as claimed in claims 1 to 7 wherein after the reaction, the flow of the methane gas into the CVD reactor was stopped and the system was then cooled under argon atmosphere.

9. The process as claimed in claims 1 to 8 wherein Graphene nanomaterials thus formed were purified and dried in an oven subsequently the Graphene nanomaterials was then grinded into fine powder using a ball mill.

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Figure 2

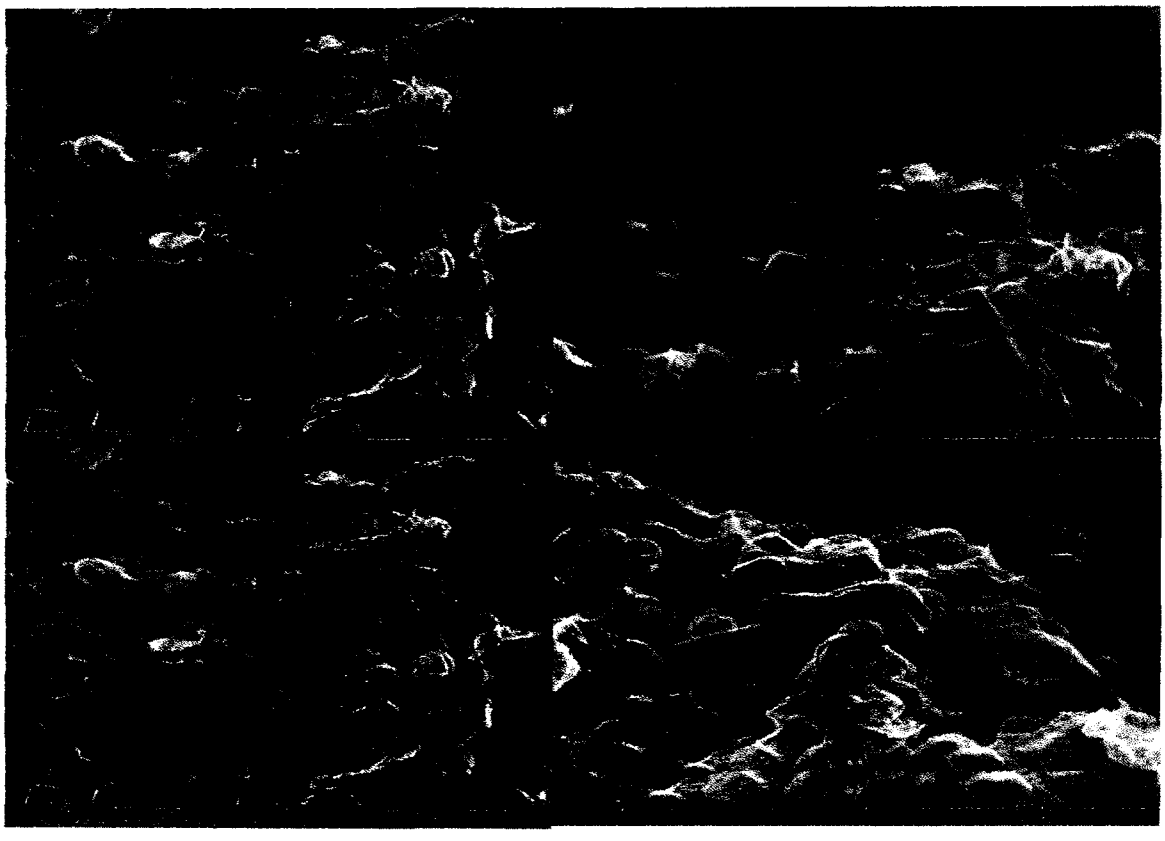

Figure 3

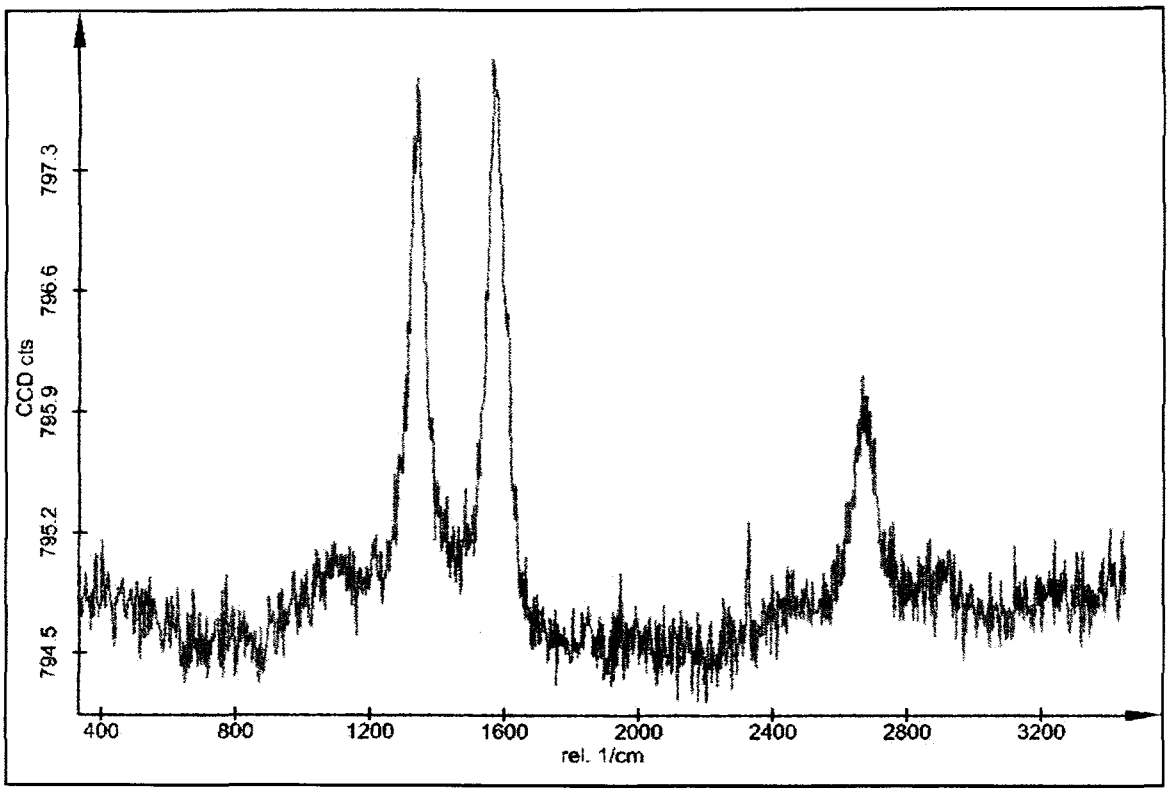
CCD cts
794.5
795.2
785.9
796.6
797.3
400
800
1200
1600
2000
2400
2800
3200
rel. 1/cm

Figure 4

Method for the Large Scale Manufacturing of Graphene Polyhedral Structures

The present invention disclosed is a method for the manufacturing of substrate free gas phase Graphene polyhedral structures. More specifically, the present invention discloses method for the large scale manufacturing of hollow, porous, multi-wall carbon nano materials of spherical and platelet like morphology synthesized by using chemical vapor disposition (CVD) of methane as precursor gas and a mixture of alkaline earth metal and transition metal catalysts.

Background of the Invention

In recent years, Graphene has become the newly attractive subject in nanomaterials science, because of its unique nanostructure and unusual electronic, mechanical, optical, thermal conductive properties, etc. The remarkable properties of Graphene reported so far include high values of its Young's modulus (~1,100 GPa), fracture strength (125 GPa), thermal conductivity (~5,000 W m−1K−1), mobility of charge carriers (200,000 cm^2 V^{-1} s^{-1}) and specific surface area (calculated value, 2,630 m^2 g^{-1}), plus fascinating transport phenomena such as the quantum Hall effect. Graphene and chemically modified Graphene (CMG) are promising candidates as components in applications such as energy-storage materials, 'paper-like' materials, polymer composites, liquid crystal devices and mechanical resonators.

Conventionally, Graphene is prepared by oxidation/intercalation of graphite to produce expanded oxidized graphite, followed by an exfoliation step, such as rapid heating at high temperature. Prud'homme *et. al* in the PCT application number WO 2007/047084 has shown that when mixed concentrated sulfuric and nitric acids combined with a high potassium chlorate concentration, provide very strongly oxidizing slurry for the oxidation/intercalation of graphite from which a highly exfoliated Graphene can be formed. A highly exfoliated Graphene has been disclosed

in PCT International Patent Application Publication Number WO 2008/079585, and in U.S. Patent Application Numbers US 20080171824 and US 20080039573.

One considerable disadvantage of known oxidation processes that the ultimately produced exfoliated Graphene required using large quantities of chlorate, a material that is both expensive and has the potential for forming hazardous or explosive reactions. Such disadvantages render the known processes commercially unfavorable.

Graphene also has also been synthesized by desorption of Si from SiC single-crystal surfaces, which yields a multilayered Graphene structure that behaves like Graphene and by a surface precipitation process of carbon in some transition metals.

However, the presence of lattice imperfections and oxygen functionalities on a Graphene sheet define its quality. Clean and highly ordered Graphene are preferable and exhibits extremely high room-temperature carrier mobility and thermal conductivity and these remarkable properties are very sensitive to defects and disorder. It has been observed that the formation of defects on pristine sheets results in electrically and thermally insulating behavior. Furthermore, the bonding of oxygen to Graphene in the form of functional groups, such as carboxyl and hydroxyl, has a detrimental effect on its electronic structure. For example, Graphene is a nearly metallic material while Graphene oxide is an insulator.

The known methods for the production of Graphene are not appropriate for the large scale manufacturing in a cost effective manner. Therefore there is a need to provide a reliable and well-controlled method for the large scale production of Graphene nano sheets.

The present invention discloses a novel substrate free Chemical Vapor Deposition (CVD) method to generate large volume of Graphene high purity using methane as precursor gas and a mixture of alkaline and transition metal as catalyst. The nano-size Graphene sheets formed in the present invention have hollow, porous, few layered carbon nanospheres or platelet like structures with a narrow size distribution and an average particle size of approximately 80 nm and an average aspect ratio close to 7:5.

Summary of the Invention

It is an object of the present invention to provide a large scale manufacturing process for the production of Graphene polyhedral structures.

It is another object of the present invention to provide a cost effective and efficient industrial scale method for the manufacture of Graphene nanomaterials

It is yet another object of the present invention to provide a Chemical Vapor Disposition (CVD) method for the production of Graphene polyhedral structure or nano-sized Graphene sheets in a substrate free environment.

In order to achieve the aforementioned objectives the present invention discloses a method for manufacturing of large scale Graphene polyhedral structure or nano sheets using a methane gas as the carbon source and a mixture of alkaline earth metal and transition metal as catalyst. The alkaline earth metal and transition metals and transition metal as catalyst preferably Fe:Co:Mg. The required amount of catalyst was loaded in Chemical Vapor Dispersion (CVD) reactor. The chamber is evacuated with vacuum at first and purged with argon gas initially. Once the furnace comes to niche temperature, methane gas is purged into the reactor vessel along

with argon gas. The flow rate of the methane gas is maintained for a period of time corresponding to the amount of catalyst loaded in the CVD reactor.

After the reaction, the flow of the methane gas into the CVD reactor was stopped and the system was then cooled under argon atmosphere. The Graphene nanomaterials thus formed were purified and dried in an oven . Subsequently, the Graphene nanomaterials was then grinded into fine powder using a ball mill .Thus very fine black, randomly aggregated few layered thin Graphene polyhedral structures of spherical and platelet like morphology was obtained.

The best mode method can be understood by following process parameters:
Carbon source: Methane gas
Catalysts: mixture of alkaline earth metal and transition metal , preferably Fe:Co:Mg in a preferred ratio of 1:1:38. The required amount of catalyst 50 gm was loaded in Chemical Vapor Dispersion (CVD) reactor. The chamber is evacuated with vacuum at first and purged with argon gas initially for example 60° C at a flow rate of 500ml/minute. Once the furnace come to niche temperature at around 1000 ° C at a slow heating rate of 4°/minute.
After the reaction, the flow of the methane gas into the CVD reactor was stopped and the system was then cooled under argon atmosphere- cooling conditions need to be specified. The Graphene nanomaterials thus formed were purified and dried in an oven – preferably at 130 °C. Subsequently, the Graphene nanomaterials was then grinded into fine powder using a ball mill. Thus very fine black, randomly aggregated few layered thin Graphene polyhedral structures of spherical and platelet like morphology was obtained. A preferred configuration of 1-2 micron to 80 nm icron hence obtained after grinding.

Brief Description of the Drawings

The following figures show the results of various characterizations carried out on the Graphene polyhedral structures

Figure 1 shows an exemplary overall approach for producing Graphene polyhedral structures in accordance with the present invention.

Figure 2 shows the Transmission Electron Microscopy (TEM) image of the Graphene polyhedral structures thus manufactured according to an embodiment of the present invention.

Figure 3 shows the Scanning Electron Microscopy (SEM) image of the Graphene polyhedral structures thus manufactured according to an embodiment of the present invention.

Figure 4 shows the Raman Spectrum of the Graphene polyhedral structures thus manufactured according to an embodiment of the present invention.

Detailed Description of the Invention

The term "Graphene" as used herein is defined as "Graphene (or '2D graphite') is a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities. It can be wrapped up into 0D fullerenes, rolled into 1D nanotubes or stacked into 3D graphite.

In a Graphene plane, carbon atoms occupy a 2-D hexagonal lattice. These carbon atoms are bonded together through strong covalent bonds lying on this plane. In the c-axis direction, several Graphene planes may be weakly bonded together primarily through van der Waals forces".

The present invention would now be described with reference to the accompanying drawings. The drawings are being used to illustrate the inventive concept and do not intend to limit the invention to the embodiments shown in them.

Figure 1 shows an exemplary overall approach, **10,** for manufacturing of large scale substrate free Graphene using Chemical Vapor Deposition (CVD) method in accordance with the present invention.

The present invention discloses a gas phase substrate free method for production of Graphene using a mixture of alkaline earth metal and transition metal catalyst. A closed chamber with alumina plates was used as the Chemical Vapor Deposition (CVD) reactor (**20**). The catalyst was loaded (**22**) in alumina plate and placed in the CVD reactor. The chamber was evacuated with vacuum at first and purged with argon gas (**24**) initially.

Once the furnace temperature reaches the niche temperature (1000 dgree C @temperature rise of 4 degree C/minute) methane gas was purged into the CVD reactor vessel (**26**) along with argon. The flow rate of the methane gas (1.2 litre /minute of methane alongwith 500 ml/minute of argon) was maintained for a period of time corresponding to the amount of catalyst loaded in the CVD reactor. The methane gas purged inside the CVD reactor was reduced to the pure carbon form, i.e., Graphene (**28**), by the alkaline and transition metal catalyst.

After the completion of reactionthe flow of the methane gas into the vessel was stopped and then the system was cooled under argon atmosphere cooling is done by continued argon gas flow @500ml/minute for another 2 hours and water circulation is continued for another 4 hours]. The nanomaterials thus formed were

purified (**32**) by one-step HCl demineralization process and further repeated washing with DM water and ethanol in a custom designed washing system assisted with centrifuge The Graphene cake was finally dried in an oven at 130°C for 12 hours (**36**) and then grinded into fine powder using a ball mill (**34**).Thus ultrafine powder of very fine black, randomly aggregated few layered thin Graphene polyhedral structures was obtained.

In an embodiment of the present invention, the Graphene polyhedral structure thus obtained have average particle size of 80nM, average aspect ratio of 7:5, and thickness of less than 6nM. Further, the average length to width and thickness ration of the Graphene polyhedral structures thus manufactured are of the order of 7:5 and 15:1 respectively.

Subsequently, the structural analysis and characterization (**38**) of the Graphene was performed using the transmission electron microscopy (TEM), scanning electron microcopy (SEM) and Raman spectroscopy. The transmission electron microscopy (TEM) studies were carried out to determine the exact size of as-manufactured Graphene polyhedral structure using Philips, TECHNAI FE 12 microscope (TEM) at an accelerating voltage of 120 kV. **Figure 2** and **Figure 3** shows the (**TEM**) image and the scanning electron microscopy (**SEM**) image of the as-manufactured Graphene polyhedral structure. Figure 4 shows a typical Raman spectrum of Graphene thus formed in the present invention. The three intense peaks were observed as the D band at 1350 cm^{-1}, the G band at 1580 cm^{-1} and the 2D band at 2650 cm^{-1}. The element analysis of the Graphene polyhedral structure thus manufactured shows the carbon content of 97.5% and oxygen content of 2.4%, which may be due to absorption from the atmosphere on to the Graphene sheets, and 0.1% impurities.

Various other embodiments are possible within the spirit of the invention and the aforementioned examples and embodiments are just meant to be for explanatory purposes, and in no way intend to bind the invention in any manner. The invention intends to cover all the equivalent embodiments and is limited only by the appended claims.