The nano-composites are useful for producing electrodes, especially for battery and supercapacitor applications.

Declarations under Rule 4.17:
— as to the identity of the inventor (Rule 4.1.7(i))
— as to applicant’s entitlement to apply for and be granted a patent (Rule 4.1.7(ii))
— as to the applicant’s entitlement to claim the priority of the earlier application (Rule 4.1.7(iii))
— as to inventorship (Rule 4.1.7(iv))

[Continued on next page]

(54) Title: PROCESS OF DRY MILLING PARTICULATE MATERIALS

(57) Abstract: Graphene produced by media ball milling has very small particle size, a relatively high surface area and unique aspect ratios. It is uniquely suited to make nano-composites or coating by coating or admixing other particles. Metals or metal oxides can be coated or formed into composites with the high surface area, relatively low aspect ratio graphene. If the added particles are larger than the graphene, they are coated with graphene, and if they are about the same approximate size, a nano-composite forms. The nanocomposites are useful for producing electrodes, especially for battery and supercapacitor applications.
Published:

— with international search report (Art. 21(3))
PROCESS OF DRY MILLING PARTICULATE MATERIALS

TO WHOM IT MAY CONCERN:
Be it known that we, Inhwan Do, residing in the City of East Lansing, County of Ingham, State of Michigan, a citizen of the Republic of Korea, Michael Knox, residing in the City of East Lansing, County Ingham, State of Michigan, a citizen of the United States of America, Scott Murray, residing in the City of East Lansing, County of Ingham, State of Michigan, a citizen of the United States of America, and Robert M. Privette, residing in the City of East Lansing, County of Ingham, State of Michigan, a citizen of the United States of America, have invented a new and novel PROCESS OF DRY MILLING PARTICULATE MATERIALS the following of which is a specification therefor.

BACKGROUND OF THE INVENTION

This invention deals with graphene platelet nano composites with metal or metal oxide, and graphene platelet nano coated with metal or metal oxide. The coated and composited particles are useful as electrodes and for electrical applications.

Graphite is formed by many layers of carbon in highly structured platelets. These platelets, when separated from the graphite superstructure, are collectively called graphene. Graphene has interesting chemical, physical, and electrical properties. These properties make graphene a highly valued product. The quality of the graphene, as defined by particle diameter, particle width, and surface area, determine its industrial utility. It is advantageous to coat or composite graphene with metal particles for electrical applications.

Xg Sciences, Inc. headquartered in Lansing, Michigan produces a "C" grade graphene by a high energy, plastic media, dry, mechanical milling process. Grade size characteristics make it uniquely suited to coating or mixing with nanoparticles to form useful materials for electrodes.
The applicant is aware of U.S. Patent publication 2011/0111303 A1 that published on May 12, 2011 as showing a wet process for treating graphene with silicon.

Also, the patentees are aware of EP2275385 in the name of Peukert, et al in which a wet process is set forth for grinding particulate materials, wherein the grinding media is yttrium stabilized zirconia.

**SUMMARY OF THE INVENTION**

Graphene produced by media ball milling has very small particle size with a relatively high surface area. It is uniquely suited to make nano-composites or coatings by coating or admixing other particles. Metals or metal oxides can be coated or formed into composites with the high surface area, relatively low aspect ratio graphene. It is believed by the inventors herein that the materials of this invention have unique aspect ratios. Ground graphite admixed with silicon has an aspect ratio fairly close to 1, graphene from a GO process, epitaxially grown graphene, or graphene from an intercalated – heating process has a very high aspect ratio. The moderate aspect ratio graphene of this invention better coats 1 to 4 micron particles and better mixes with even small nano-particles.

Based on Raman spectroscopy with the aspect ratio, particle size, and/or surface area, provides graphene in this invention that is unique.
Based on the following table calculated from Raman Spectroscopy and measuring peak height, generated the following table.

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<th>G</th>
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</table>

Native graphite has a very high G/D ratio. Graphite ground to amorphous powder has the G/D ratio, the material of the instant invention starts high and tends toward 2 the more the material is processed. Amorphous graphite also has a G peak red shift to 2000 cm⁻¹. The material of the instant invention may have a small red shift, but from the quality of the data it is hard to determine. The very high surface area and aspect ratio confirms it is largely graphene nano-platelets.

Mechanically exfoliated graphene is distinct from ground graphite, in that, it maintains the strong crystalline sp² structure. As graphite is ground to amorphous, the ratio of G to D Raman lines tends to 2 and the G line red shifts from 1560 cm⁻¹ to 2000 cm⁻¹. The G peak is referred to as the graphene peak. The D peak referred to as the Disorder peak. The more graphite is ground, the more the G peak is reduced and the D peak is increased.

If the added particles are larger than the graphene, they are coated with graphene, and if they are about the same approximate size, a nano-composite forms. The nanocomposites are useful for producing electrodes, especially for battery and capacitor applications.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 is a graph of battery performance of a Si/graphene (200-250 m²/g, 100 minutes processing time).
THE INVENTION

Thus, in one embodiment, there is a process of dry milling particulate materials, wherein at least one of the particulate materials is a layered material, in the presence of a non-layered material, to obtain a composition wherein the layered material is exfoliated and wherein the non-layered material is composited with the exfoliated material.

The exfoliated material has a particle size of 10 microns by 5 nm thick, or less. In addition, the dry milling is controlled by controlling the surface energy of the milling media in addition to controlling the hardness of the milling media.

In a second embodiment, that is a process of dry milling particulate materials, wherein at least one of the particulate materials is a layered material, in the presence of a particulate material selected from the group consisting of i. ceramic, ii. glass, and iii. quartz, to obtain a composition wherein the layered material is exfoliated and wherein the particulate material is coated with the exfoliated material.

The exfoliated material has a particle size of 500 nanometers or less. In addition, the dry milling is controlled by controlling the surface energy of the milling media in addition to controlling the hardness of the milling media.

In a fourth embodiment, there is a composited product obtained by the first embodiment and a coated product obtained by the second embodiment.

DETAILED DESCRIPTION OF THE INVENTION

The graphene produced by the methods of this invention has a relatively narrow aspect ratio, greater than graphite. For this invention aspect ratios above 5 and below 200 are preferred and more preferred are aspect ratios above 10 and below 25.
The small, that is, 1 to 5 nanometers thick, and 50 to 100 nanometers diameter, high surface area (above 500 BET), medium aspect ratio graphene, is a unique size for coating with small metal or metal oxide particles.

The metals useful in this invention are the metalloid silicon, and the metals tin, iron, magnesium, manganese, aluminum, lead, gold, silver, titanium, platinum, palladium, ruthenium, copper, nickel, rhodium, and alloys of any of the above.

The plastic milling media useful in this invention has a hardness on the Brinell Scale in the range of 3 to 100. The plastic milling media is selected from the group consisting essentially of polyacetals, polyacrylates, such as, for example, methylmethacrylate, polycarbonate, polystyrene, polypropylene, polyethylene, polytetrafluoroethylene, polyethylene-imide, polyvinylchloride, polyamine-imide, phenolics and formaldehyde-based thermosetting resins, and alloys of any of the plastics named.

The particulate metal oxides useful in this invention are metal oxides selected from silicon, tin, iron, magnesium, manganese, aluminum, lead, gold, silver, titanium, platinum, palladium, ruthenium, copper, nickel, rhodium, tungsten, cobalt, molybdenum, and alloys of any of the above named metal oxides, wherein the metal and metal oxide particles have a size of 100 microns or less. Preferred are particle sizes of 10 microns or less, and most preferred are particle sizes of 5 microns or less.

Metal carbides, metal nitrides are useful in this invention, as well as non-layered materials.

Graphene useful in this invention is preferred to have a thickness of 5 nm or less.

Examples
Example 1
Two grams of natural graphite and 1 g of micron sized Si (1 to 4 \textmu m) were loaded into a 65 ml stainless steel grinding container and milled in the presence of 24 g of polymethylmethacrylate balls. The polymethylmethacrylate balls consisted of two different sizes, namely, 1/4 inches and 3/8 inches in diameter. The high energy milling machine was operated at < 1500 rpm and its clamp speed was 1060 cycle/min. The polymethylmethacrylate balls can be replaced with polycarbonate, polystyrene, polypropylene, polyethylene, polytetrafluoroethylene, polyethyleneimide, polyvinylchloride and polyamide-imide to control milling efficiency, graphene size, porosity distribution and surface area at a fixed milling time, contact quality between Si and graphene surface. The surface area of the Si/graphene composite produced can be varied from 100 \text{m}^2/\text{g} to 700 \text{m}^2/\text{g} depending on milling time (60 to 500 min.) and Si/graphene composition and type of ball materials.

The result for the battery performance of a Si/graphene (200 to 250 \text{m}^2/\text{g}, 100 min. processing) sample as an anode for a lithium ion battery is plotted infra. The Si/graphene shows high capacity (>800 mAh/g, electrode loading) over 35 cycles at 100 mA/g, which supports the low cost, simple, time-saving, environmentally benign, flexible way to produce high performance graphene-based composite materials for energy applications. Some fluctuation of the capacity is due to the variation of temperature.

Example 2
Two grams of natural graphite and 1 g of nano sized metal oxides (Fe$_2$O$_3$, NiO, CoO$_3$, MnO$_3$) were loaded in a 65 ml stainless steel grinding container and milled in the presence of 24 g of polymethylmethacrylate balls. The products can be used as anode
materials for lithium batteries and electrodes for supercapacitors.
What is claimed is:

1. A process of dry milling particulate materials, wherein at least one of the particulate materials is a layered material, in the presence of a non-layered material, to obtain a composition wherein the layered material is exfoliated and wherein the non-layered material is composited with the exfoliated material, the exfoliated material having a particle size of 10 microns by 5 nm thick, or less, and wherein the dry milling is controlled by controlling the surface energy of the milling media in addition to controlling the hardness of the milling media.

2. The process as claimed in claim 1 wherein the non-layered material is selected from the group consisting essentially of:
   
   i. a particulate metal and,
   
   ii. a particulate metal oxide.

3. The process as claimed in claim 1 wherein the layered material is graphite.

4. The process as claimed in claim 1 wherein the milling media has a surface energy essentially equivalent to the surface energy of the layered material.

5. The process as claimed in claim 1 wherein the milling media has a hardness on the Brinell Scale in the range of 3 to 100.

6. The process as claimed in claim 1 wherein the exfoliated material has an aspect ratio of greater than about 25.

7. The process as claimed in claim 1 wherein the exfoliated material has an aspect ratio of from 5 to 200.

8. The process as claimed in claim 1 wherein the exfoliated material has a size in the range of from 50 nm to 10 microns.
9. The process as claimed in claim 1 wherein the exfoliated material has a thickness of from 1 μm to 5 μm.

10. The process as claimed in claim 1 wherein the milling media is plastic material.

11. The process as claimed in claim 10 wherein the plastic is selected from the group consisting essentially of:
   i. polymethylmethacrylate,
   ii. polycarbonate,
   iii. polystyrene,
   iv. polypropylene,
   v. polyethylene,
   vi. polytetrafluoroethylene,
   vii. polyethyleneimide,
   viii. polyvinylchloride,
   ix. polyamine-imide, and,
   x. alloys of any of i. to ix.

12. The process as claimed in claim 2 wherein the particulate metals are selected from the group consisting essentially of:
   i. silicon,
   ii. tin,
   iii. iron,
   iv. magnesium,
   v. manganese,
   vi. aluminum,
   vii. lead,
   viii. gold,
   ix. silver,
   x. titanium,
   xi. platinum,
   xii. palladium,
   xiii. ruthenium,
xiv. copper,
xv. nickel,
xvi. rhodium, and,
xvii. alloys of any of i. to xvi.

13. The process as claimed in claim 2 wherein the particulate metal oxides are selected from the group consisting essentially of oxides of:

i. silicon,
ii. tin,
iii. iron,
iv. magnesium,
v. manganese,
vi. aluminum,
vii. lead,
viii. gold,
ix. silver,
x. titanium,
xi. platinum,
xii. palladium,
xiii. ruthenium,
xiv. copper,
xv. nickel,
xvi. rhodium, and,
xvii. alloys of any of i. to xvi.

14. The process as claimed in claim 1 wherein the particulate non-layered material has a size less than 100 microns.

15. The process as claimed in claim 1 wherein the particulate are metal carbides.

16. The process as claimed in claim 1 wherein the particulate materials are metal nitrides.

17. A product when produced by the process of claim 1.
18. An electrode produced from the product as claimed in claim 17.
19. A catalyst produced from the product as claimed in claim 17.
20. A coating produced from the product as claimed in claim 17.
21. An electronic component manufactured from the product as claimed in claim 17.
22. A thermally conductive component manufactured from the product as claimed in claim 17.
23. A process of dry milling particulate materials, wherein at least one of the particulate materials is a layered material, in the presence of a particulate material selected from the group consisting of i. ceramic, ii. glass, and iii. quartz, to obtain a composition wherein the layered material is exfoliated and wherein the particulate material is coated with the exfoliated material, the exfoliated material having a particle size of 500 nanometers or less, and wherein the dry milling is controlled by controlling the surface energy of the milling media in addition to controlling the hardness of the milling media.
24. A process of dry milling particulate materials, wherein at least one of the particulate materials is a layered material, in the presence of a particulate material selected from the group consisting of i. ceramic, ii. glass, and iii. quartz, to obtain a composition wherein the layered material is exfoliated and wherein the particulate material is coated with the exfoliated material, the exfoliated material having a particle size of 10 microns or more, and the wherein the dry milling is controlled by controlling the surface energy of the milling media in addition to controlling the hardness of the milling media.
energy of the milling media in addition to controlling the hardness of the milling media.

25. A composition of matter comprising particles compositon with graphene wherein the particles are selected from the group consisting essentially of metal particles, and metal oxide particles, wherein the metal and metal oxide particles have a size of 100 microns or smaller.

26. A composition of matter as claimed in claim 25 wherein the metal and metal oxide particles have a size of 100 microns or less.

27. A composition of matter as claimed in claim 25 wherein the metal and metal oxide particles have a size of 10 microns or less.

28. A composition of matter as claimed in claim 25 wherein the metal and metal oxide particles have a size of 1 micron or less.

29. A composition of matter as claimed in claim 25 wherein the graphene is less than 5 nm thick.

30. A composition of matter as claimed in claim 25 wherein the graphene is a monolayer thick.

31. A composition of matter as claimed in claim 25 wherein the oxygen content of the graphene is ten atomic weight percent or less.

32. A composition of matter as claimed in claim 25 wherein the metal is selected from the group consisting essentially of iron, magnesium, cobalt, molybdenum, and lead.

33. A composition of matter as claimed in claim 25 wherein the metal oxide is selected from the group of oxides consisting essentially of iron oxide, magnesium oxide, cobalt oxide, molybdenum oxide, and lead oxide.

34. A composition of matter as claimed in claim 25 wherein the size of the graphene particle is less than 5 microns.
35. A composition of matter as claimed in claim 25 wherein the surface area of the graphene is greater than about 300 m²/g BET.

36. A composition of matter as claimed in claim 25 wherein the metal particles are larger than the graphene composited with them.

37. A composition of matter as claimed in claim 25 wherein the metal particle are essentially the same size as the graphene they are combined with.

38. A composition of matter as claimed in claim 25 that is a nanocomposite.

39. An electrode manufactured from the composition of claim 25.

40. A battery comprising at least one electrode as claimed in claim 39.

41. A capacitor comprising an electrode as claimed in claim 39.
Si/milled graphene composite anode
8.2mg total active material,
4.6mg/cm² loading
2.5mg Si total, 1.4mg Si/cm²
CR2016

FIG 1
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

B02C 17/20(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B02C 17/20; B32B 9/00; H01M 4/62; H01M 4/50; C01G 25/02; C04B 35/563; C04B 35/565; H01M 4/04; H01M 4/58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & keywords: milling, dry, media ball, nano composites, graphene, metal, silicon, electrode

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

See patent family annex.

Date of the actual completion of the international search

09 August 2013 (09.08.2013)

Date of mailing of the international search report

12 August 2013 (12.08.2013)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office

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Form PCT/ISA/210 (second sheet) (July 2009)
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