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(71) Applicant: **UNIVERSITI PUTRA MALAYSIA** [MY/MY]; Putra Ip Division, Putra Science Park, Office of the Deputy Vice Chancellor (Research and Innovation), Universiti Putra Malaysia, 43400 Serdang, Selangor Malaysia, Selangor, 43400 (MY).

(72) Inventors: **ABDUL RASHID, Suraya**; Institute Of Advanced Technology (ITMA), Universiti Putra Malysia 43400 Serdang Selangor Malaysia, Selangor, 43400 (MY). **JAMALUDIN, Norhanisah**; Institute Of Advanced Technology (ITMA), Universiti Putra Malaysia 43400 Serdang Selangor Malaysia, Selangor, 43400 (MY). **YOSHIDA, Hiroyuki**; Department of Chemical & Environmental Engineering, Fakulti Kejuruteraan, Universiti Putra Malaysia 43400 Serdang Selangor Malaysia, Selangor, 43400 (MY).

(74) Agent: **YIP, JIUN HANN**; TRADEMARK2U SDN BHD (670910-M) NO. 1, Block C, Jalan Dataran SD 1, Dataran SD PJU 9, Bandar Sri Damansara 52200 Kuala Lumpur Malaysia, Kuala Lumpur, 52200 (MY).

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(54) Title: PREPARATION OF CARBON QUANTUM DOTS

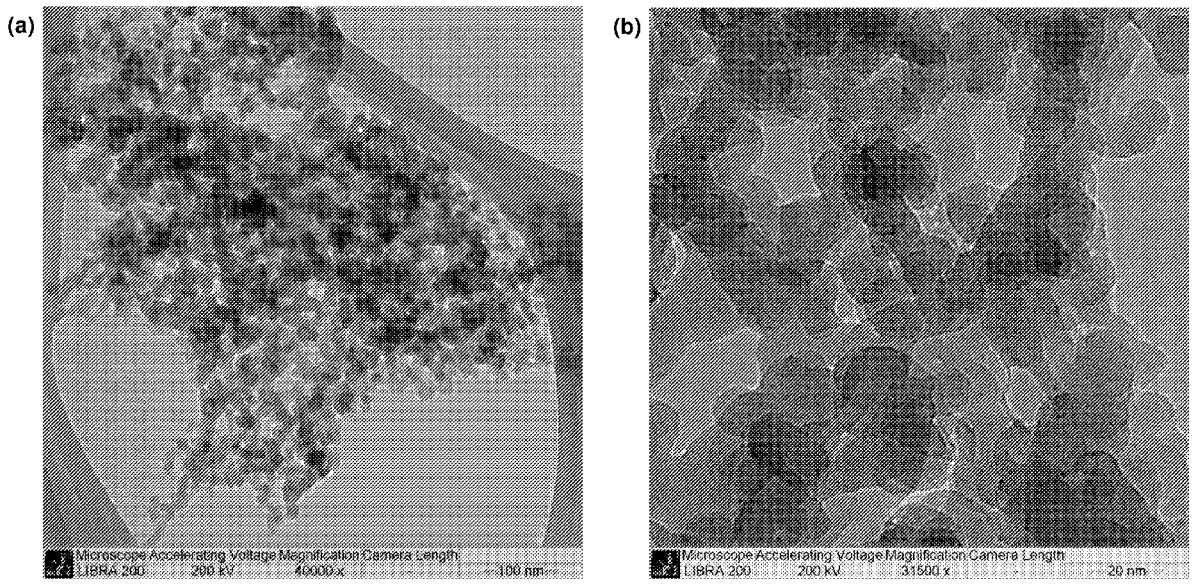

Fig. 1

(57) Abstract: The present invention relates to a method of preparing carbon quantum dots (CQD), characterised by: dispersing carbonaceous particles in absolute alcohol or a mixture of water and alcohol; and heating the dispersion to obtain photoluminescent liquid comprising the CQD.

[Continued on next page]

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PREPARATION OF CARBON QUANTUM DOTS

Background of the Invention

Field of the Invention

This invention relates to a method of preparing carbon quantum dots, and more particularly an acid-free method for carbon quantum dots preparation.

Description of Related Arts

Carbon quantum dots (CQD or C-dots) are nanosized fragments of carbon typically less than 10 nanometers in size. CQD is a generic term for carbon fragments having any particular shape. Usually CQD prepared from a bottom-up approach would have spherical structures whereas CQD prepared from a top-down approach would have planar structures. CQD having planar structures are also known as Graphene Quantum Dots (GQD). CQD prepared from graphite or graphite-like or graphitized material are also known as GQD. CQD are categorised as zero dimensional nanostructures having high surface area and photoluminescent properties. These characteristics render them as promising material in various applications, such as energy storage, catalysts, and sensors. Furthermore, in their pure carbon form they are non-toxic if compared to their conventional metal counterparts.

GQD is usually synthesised by a top-down approach, which starts with large fragments and the fragments are chemically oxidised to reduce the size. The top-down approach is popular because GQD has been found during the ubiquitous preparation of graphene oxide from graphite by chemical oxidation. Using the same approach, graphite can also be substituted with various types of carbonaceous starting materials, for example, charcoals and biochars.

Chemical oxidation processes use large amounts of acids and oxidising agents. Moreover, bases are used for the neutralisation of acids. However, the use of hazardous chemicals is undesirable, especially for large scale production. The

neutralisation process in turn, produces large amounts of salts that need washing. The washing of GQD requires a tedious dialysis process as the small sized GQD have to be handled with extreme care. Despite the aforementioned drawbacks, chemical oxidation process is routinely used because of its effectiveness in GQD production.

An example of the method of making GQD using an oxidant is disclosed in WO 2014/179708. In this prior art, the GQD is formed by exposing a carbon source to the oxidant, which may include an acid. Separation of the formed GQD from the oxidant is then performed by neutralisation, filtration, and dialysis.

Recently alternative approaches have been used to produce GQD by using different chemicals, such as oxone (Shin, Y. *et al.*, 2015) and sodium hypochlorite (Zhou, X. *et al.*, 2016). However, the use of these chemicals can also lead to harmful complications.

Accordingly, it can be seen in the prior arts that there exists a need to provide a safe, acid-free, and simple method for large scale production of CQD.

References

- Shin, Y. *et al.*, Acid-free and Oxone Oxidant-assisted Solvothermal Synthesis of Graphene Quantum Dots using Various Natural Carbon Materials as Resources, *Nanoscale*, 2015, 7, 5633-5637.
- Zhou, X. *et al.*, Large Scale Production of Graphene Quantum Dots Through the Reaction of Graphene Oxide with Sodium Hypochlorite, *RSC Advances*, 2016, 54644-54648.

Summary of Invention

It is an objective of the present invention to provide an acid-free method for preparing CQD.

It is also an objective of the present invention to provide a non-toxic method for preparing CQD.

It is yet another objective of the present invention to provide a simple method for large-scale production of CQD.

Accordingly, these objectives may be achieved by following the teachings of the present invention. The present invention relates to a method of preparing CQD, characterised by: dispersing carbonaceous particles in absolute alcohol or a mixture of water and alcohol; and heating the dispersion to obtain photoluminescent liquid comprising the CQD.

Brief Description of the Drawings

The features of the invention will be more readily understood and appreciated from the following detailed description when read in conjunction with the accompanying drawings of the preferred embodiment of the present invention, in which:

Fig. 1 (a) and (b) are HRTEM images of CQD obtained from coconut shell biochar at different magnifications.

Fig. 2 show CQD suspensions prepared at 250 °C using starting samples of (from left to right) coconut shell biochar, kenaf biochar and EFB biochar (a) under ambient light (b) under UV light (365 nm).

Fig. 3 is a graph illustrating the photoluminescent spectra for a CQD suspension prepared from EFB biochar at 250°C.

Detailed Description of the Invention

As required, detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely exemplary of the invention, which may be embodied in various forms. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting but merely as a basis for claims. It should be understood that the

drawings and detailed description thereto are not intended to limit the invention to the particular form disclosed, but on the contrary, the invention is to cover all modifications, equivalents and alternatives falling within the scope of the present invention as defined by the appended claims. As used throughout this application, the word "may" is used in a permissive sense (i.e., meaning having the potential to), rather than the mandatory sense (i.e., meaning must). Similarly, the words "include," "including," and "includes" mean including, but not limited to. Further, the words "a" or "an" mean "at least one" and the word "plurality" means one or more, unless otherwise mentioned. Where the abbreviations or technical terms are used, these indicate the commonly accepted meanings as known in the technical field. For ease of reference, common reference numerals will be used throughout the figures when referring to the same or similar features common to the figures. The present invention will now be described with reference to Figs. 1-3.

The present invention relates to a method of preparing carbon quantum dots (CQD), characterised by:

dispersing carbonaceous particles in absolute alcohol or a mixture of water and alcohol; and

heating the dispersion to obtain photoluminescent liquid comprising the CQD.

In a preferred embodiment of the method of preparing the CQD, the carbonaceous particles are selected from a group comprising graphite or graphite-like materials including coal, biochar, or a combination thereof.

In a preferred embodiment of the method of preparing the CQD, the alcohol is selected from a group comprising ethanol, methanol, propanol, isopropanol, or a combination thereof.

In a preferred embodiment of the method of preparing the CQD, the dispersion is heated at a temperature below the critical point of water.

In a preferred embodiment of the method of preparing the CQD, the temperature is in a range of 200°C to 350°C.

In a preferred embodiment of the method of preparing the CQD, the heating is performed by submerging a container containing the dispersion in a salt bath for 5 to 10 minutes.

In a preferred embodiment of the method of preparing the CQD, the carbonaceous particles are subjected to milling before the dispersion step.

In a preferred embodiment of the method of preparing the CQD, the carbonaceous particles are subjected to microwaving after the milling step.

In a preferred embodiment of the method of preparing the CQD, the microwaving is performed for up to 60 seconds for every gram of the carbonaceous particles.

Below is an example of the preparation and applications of CQD from which the advantages of the present invention may be more readily understood. It is to be understood that the following example is for illustrative purpose only and should not be construed to limit the present invention in any way.

Examples

Carbonaceous particles were ball milled to reduce the size of the particles from micrometer to nanometer. In an example of using coconut shell biochar as the carbonaceous particles, the biochar was milled for 24 hours to yield a particle size distribution of less than 500 nanometers, with about 50% being less than 200 nanometers. Then, 0.6 g of the particles were dispersed in a mixture containing water and ethanol in a ratio (by volume) of 1:1 by sonication for 15 minutes. The dispersion was then poured into a steel cylindrical container with swagelok end caps that were carefully tightened to avoid leaking. The container was immersed in a salt bath at a temperature of 250°C for five minutes. The container was removed

from the salt bath and allowed to cool down prior to the collection of the mixture. The mixture was subjected to centrifugation at 4000 rpm for five minutes to separate any remaining solids from the liquid. The liquid was then qualitatively examined for fluorescence by shining ultraviolet (UV) light onto the samples. CQD containing liquid were shown to emit blue light.

In order to improve the yield of CQD, milled particles were microwaved for one minute using a conventional microwave oven before being dispersed in the water-alcohol mixture. This helps to expand and increase the interlayer d-spacing between graphitized sheets. Table 1 shows the CQD yield obtained from coconut shell biochar under different conditions.

Table 1: Yield of CQD produced from coconut shell biochar under different conditions

Biochar	Sample	Condition	Initial powder weight, g	Final powder weight, g	Yield of suspended product, %	Fluorescence
Coconut	C1	Subcritical[a] water	0.060	0.0455	42	No
	C2	Subcritical[a] ethanol/water	0.063	0.058	7.9	Yes
	C3	Ethanol/water (sonicate[b])	0.0552	0.0059	89.3	No
	C4	Subcritical[a] ethanol/water (sonicate[b])	0.0645	0.0495	23.3	Yes
	C5	Subcritical[a] ethanol/water (sonicate[b]) + microwave[c]	0.061	0.0289	52.6	Yes

[a]Subcritical conditions: 300°C for 5 minutes

[b]Sonication time: 5 minutes

[c]Microwave time: 1 minute

Note that the yield of suspended product referred to the amount of particles suspended in the supernatant obtained after centrifuge. This liquid contained small CQD (around 10 nm) as well as relatively larger sheets of graphene platelets (200-300 nm). High-resolution transmission electron microscopy (HRTEM) images of the CQD are shown in Figures 1a and 1b.

Different types of biochar result in CQD with different photoluminescent behaviour. Examples of other types of biochar include kenaf and oil palm empty fruit bunch (EFB). Figures 2a and 2b show CQD suspensions prepared using different types of biochar at 250 °C under ambient light and UV light at 365 nm, respectively.

Quantitative analysis of the CQD was carried out using photoluminescent spectroscopy. Figure 3 illustrates the photoluminescent spectra for a CQD suspension obtained from EFB biochar prepared at 250°C.

In other embodiments, CQD prepared using different water:alcohol ratios, different types of alcohol and different types of carbonaceous particles were shown to emit light ranging from green to blue.

The electrochemical and photochemical properties of CQD find applications in the fields of energy storage (supercapacitor and dye sensitised solar cell) and biosensing platforms.

Reports on the use of CQD as electrode materials in the field of energy storage are very limited. Meanwhile, conducting polymers (CP) are well-studied pseudocapacitive material used as the electrode material for supercapacitors due to the low cost of monomers, simple synthesis process, environmental stability, and high specific pseudocapacitance. However, CP swell and contract substantially on charge and discharge, respectively. Consequently, the life cycle is poor compared with carbon-based supercapacitors. Conducting polymer/carbon quantum dot (CP/CQD) composites can be developed as new electrode material for supercapacitor as the advantages of one type could complement with the

drawbacks of another. It is expected that the synergistic effect of both materials can provide outstanding supercapacitor performance.

Low cost dye-sensitised solar cell, which is the third generation solar cell, has attracted considerable attention due to its advantages, such as cost effective, simple, and environmental friendly fabrication process. However, the synthetic dyes tailored for its visible region is not sensitive to the UV light. To overcome this problem, a stroke-shift material such as CQD is provided to contribute to quantum excitation effects that will improve the dye sensitised solar cell (DSSC) light absorption. This is achieved by incorporating CQD in the electrolytes in which the UV light is converted into visible light that can be absorbed by the dye, and thus improving the system efficiency.

CQD are excellent candidates for biosensing applications due to its photochemical properties. The CQD can be important marker molecule for monitoring uric acid level in body fluids. The existing methods involve laborious procedures, expensive reagents, and limited specificity and sensitivity. Therefore, it is necessary to develop simple, accurate, and sensitive methods for the determination of uric acid level , which can be achieved by the use of CQD conjugated dual enzymes (uricase/horseradish peroxidise). The principle of detection is based on fluorescence quenching of CQD which is induced by enzymatic reaction. This biosensing system is expected to give high sensitivity and specificity with the utilisation of CQD.

Although the present invention has been described with reference to specific embodiments, also shown in the appended figures, it will be apparent for those skilled in the art that many variations and modifications can be done within the scope of the invention as described in the specification and defined in the following claims.

Claims

I/We claim:

1. A method of preparing carbon quantum dots (CQD), characterised by:

dispersing carbonaceous particles in absolute alcohol or a mixture of water and alcohol; and

heating the dispersion to obtain photoluminescent liquid comprising the CQD.

2. The method according to claim 1, wherein the carbonaceous particles are selected from a group comprising graphite or graphite-like materials, including coal, biochar, or a combination thereof.

3. The method according to claim 1, wherein the alcohol is selected from a group comprising ethanol, methanol, propanol, isopropanol, or a combination thereof.

4. The method according to claim 1, wherein up to 1 g of the carbonaceous particles are dispersed in every 6 ml of the absolute alcohol or the mixture of water and alcohol to obtain the dispersion.

5. The method according to claim 1, wherein the dispersion is heated at a temperature below the critical point of water.

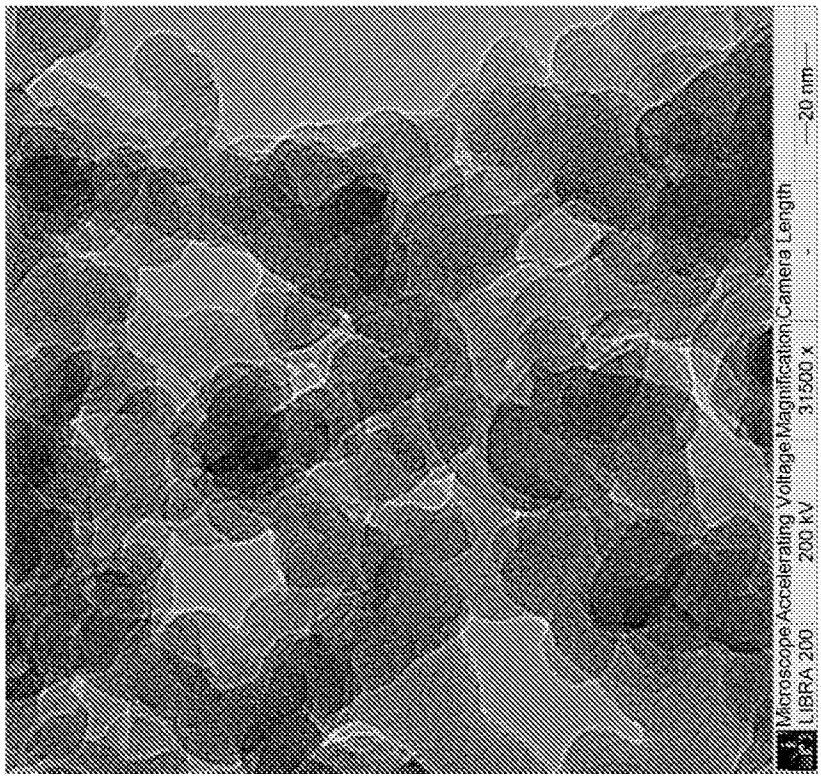
6. The method according to claim 5, wherein the temperature is in a range of 200°C to 350°C.

7. The method according to claim 6, wherein the heating is performed by submerging a container containing the dispersion in a salt bath for 5 to 10 minutes.

8. The method according to claim 1, wherein the carbonaceous particles are subjected to milling before the dispersion step.

9. The method according to claim 8, wherein the carbonaceous particles are subjected to microwaving after the milling step.

10. The method according to claim 9, wherein the microwaving is performed for up to 60 seconds for every gram of the carbonaceous particles.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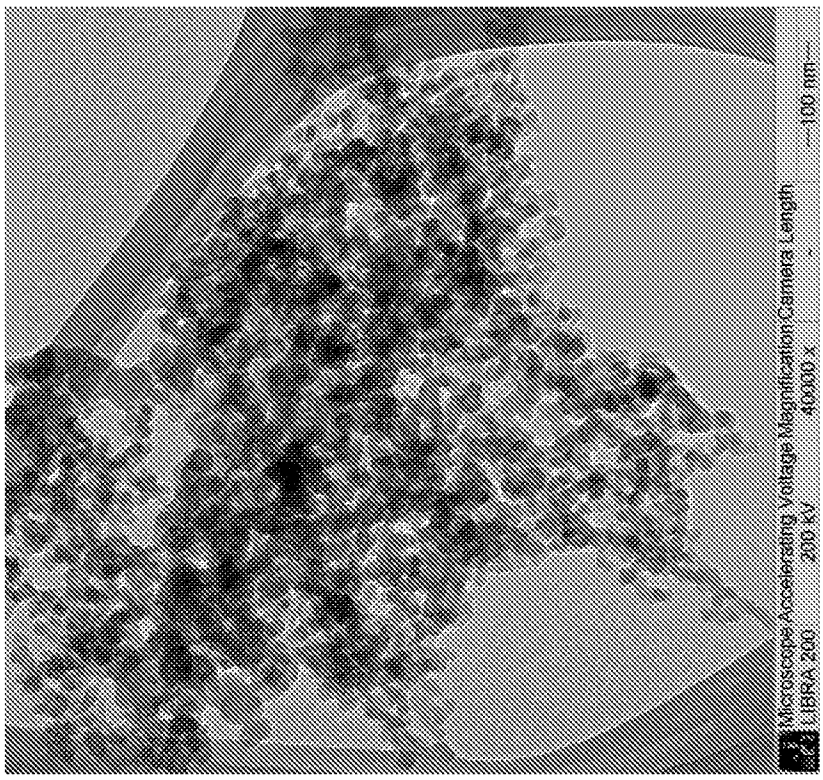
(b)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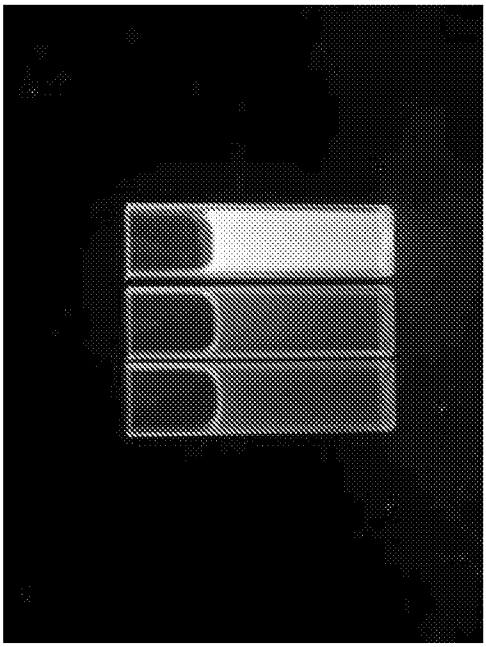
(a)

Fig. 1



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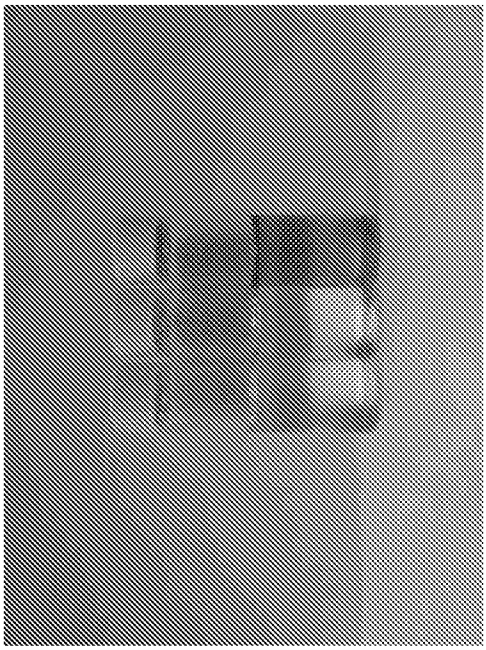

(a)

Fig. 2

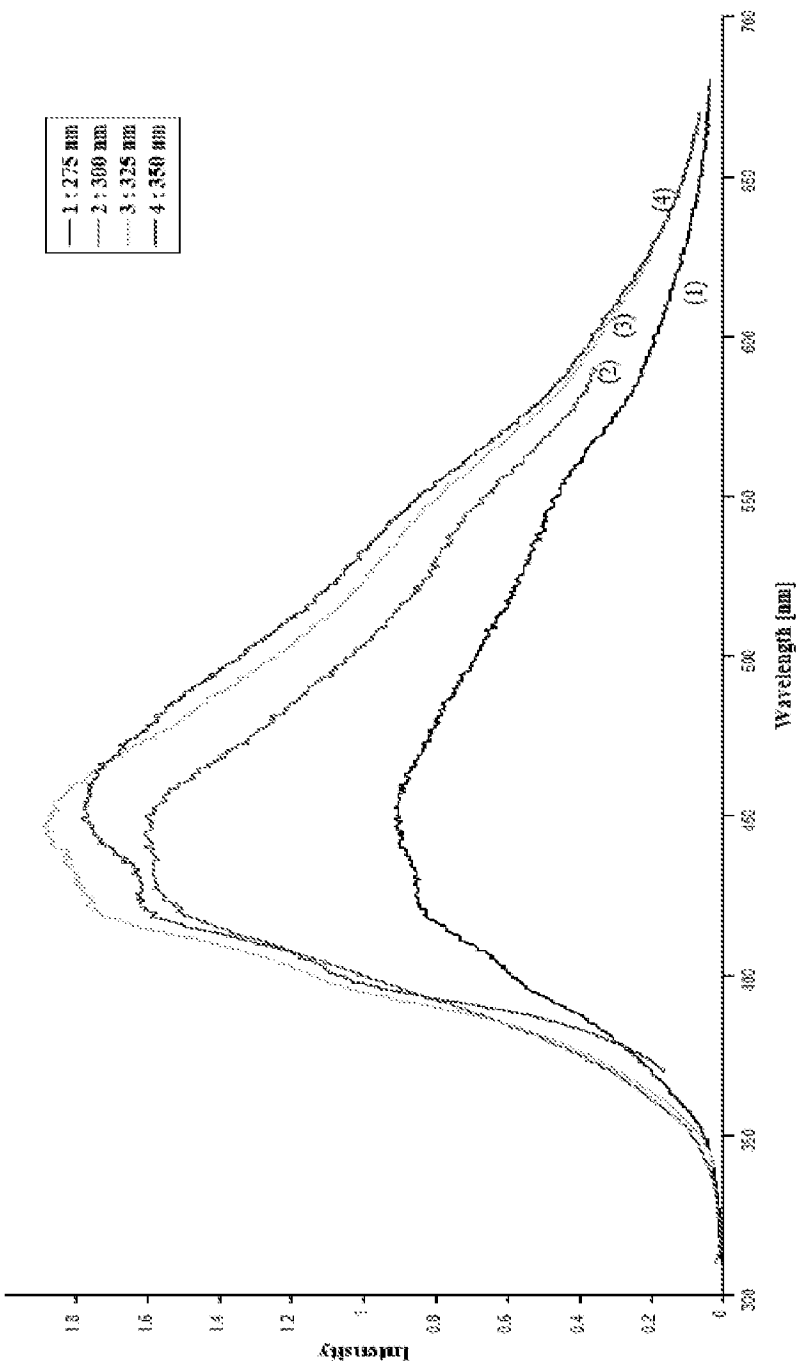

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/MY2017/050055

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C01B32/15(2017.01)i, B82Y40/00(2011.01)i, C09K11/65(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)

Int.Cl. C01B32/15, B82Y40/00, C09K11/65

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2017
Registered utility model specifications of Japan 1996-2017
Published registered utility model applications of Japan 1994-2017

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

JSTPlus/JMEDPlus/JST7580 (JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y A	CN 103980893 A (TAIYUAN UNIVERSITY OF TECHNOLOGY) 2014.08.13, Claims 1-5, Examples 1-8, 10 & CN 103980893 B	1-6 7, 8 9, 10
X Y A	WO 2015/106437 A1 (SHENZHEN CANTONNET ENERGY SERVICES CO., LTD) 2015.07.23, Examples 4, 6, 7 & US 2016/0325999 A1: Embodiment 4, 6, 7 & EP 3085665 A1 & JP 2017-510534 A	1, 2, 4-6 8-10 3, 7
Y A	US 2008/0182984 A1 (CANON KABUSHIKI KAISHA) 2008.07.31, Claims, [0057], [0058], EXAMPLES & US 7737270 B2 & JP 2008-179729 A	7-10 1-6

☑ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05.12.2017	26.12.2017

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/MY2017/050055

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2008/0113448 A1 (CLEMSON UNIVERSITY) 2008.05.15 & US 2011/0014630 A1 & US 2011/0049412 A1 & WO 2007/050984 A2 & EP 1945736 A2 & JP 2009-513798 A	1-10
A	SASIKALA, S. P. et al., High Yield Synthesis of Aspect Ratio Controlled Graphenic Materials from Anthracite Coal in Supercritical Fluids, ACS Nano, 2016.05, Vol.10, No.5, p.5293-5303, ISSN 1936-0851	1-10
A	CN 103950913 A (NANJING UNIVERSITY OF AERONAUTICS AND ASTRONAUTICS) 2014.07.30 & CN 103950913 B	1-10
A	JP 2014-19599 A (JAPAN HEALTH SCIENCES FOUNDATION) 2014.02.03 & JP 6051427 B2	1-10