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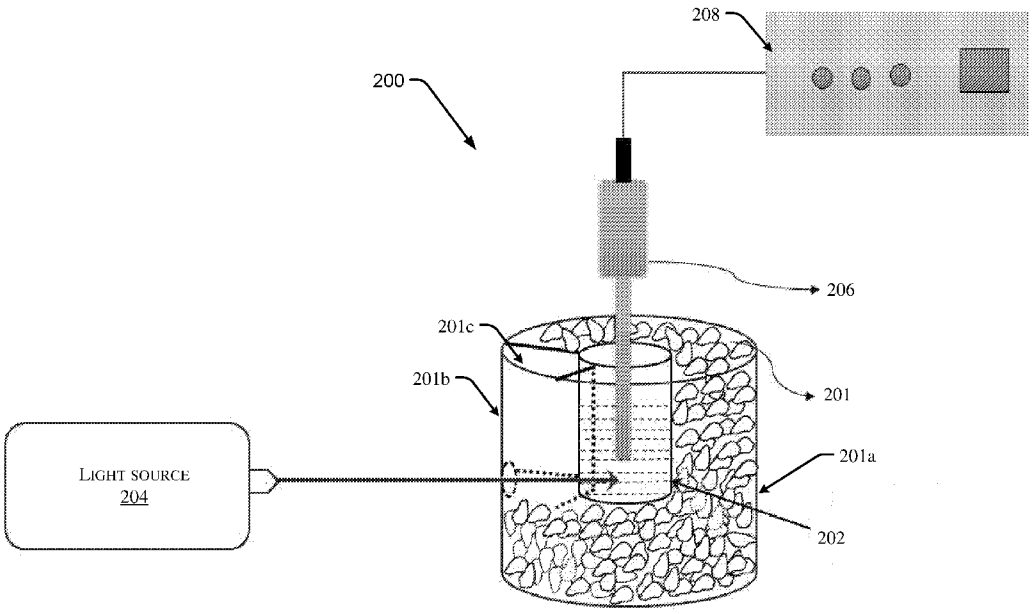

Fig. 2

(57) Abstract: A method (100) of production of nanosheets from layered bulk material is provided. The layered bulk material is contacted with a solvent to obtain a first mixture. The first mixture is simultaneously exposed to high energy density photons and mechanical shearing to obtain a first dispersion comprising residual bulk material, nanosheets, and the solvent. A first supernatant and a first residue are obtained from the first dispersion. The nanosheets can be obtained from the first supernatant by separating the nanosheets from it.

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WO 2020/141554 A1

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OPTO-MECHANICAL PRODUCTION OF NANOSHEETS FROM LAYERED MATERIALS

TECHNICAL FIELD

[0001] The present subject matter relates in general to production of nanosheets, and in particular to opto-mechanical production of nanosheets from layered materials.

BACKGROUND

[0002] Two-dimensional (2D) nanosheets provide enhanced functionalities compared to their bulk counterparts. Conventionally, nanosheets of layered materials, such as graphene, have been exfoliated from layered bulk material. Since the success of mechanically exfoliated graphene in devices, commercialisation of graphene-based applications has been achieved by large scale production of graphene. However, unlike graphene, large scale production of nanosheets of other 2D materials has remained a challenge due to its low yield factor.

BRIEF DESCRIPTION OF DRAWINGS

[0003] The detailed description is described with reference to the accompanying figures. In the figures, the left-most digit(s) of a reference number identifies the figure in which the reference number first appears. The same numbers are used throughout the drawings to reference like features and components.

[0004] Fig. 1(a) illustrates a method for production of nanosheets from layered bulk material, in accordance with an implementation of the present subject matter.

[0005] Fig. 1(b) illustrates an extended method for production of nanosheets from layered bulk material, in accordance with an implementation of the present subject matter.

[0006] Fig. 1(c) illustrates a schematic of a method for production of nanosheets from layered bulk material, in accordance with an implementation of the present subject matter.

[0007] Fig. 2 illustrates an assembly for production of the nanosheets, in accordance with an implementation of the present subject matter.

[0008] Fig. 3(a) depicts a schematic representation of exfoliation of bulk boron nitride, in accordance with an implementation of the present subject matter.

[0009] Fig. 3(b) depicts Scanning Electron Microscope (SEM) image of bulk material, in accordance with an implementation of the present subject matter.

[00010] Fig. 3(c) depicts SEM image of nanosheets obtained by using the method of the present subject matter, in accordance with an implementation of the present subject matter.

[00011] Figs. 4(a)-(d) depict SEM images of nanosheets obtained by using the method, in accordance with an implementation of the present subject matter.

[00012] Fig. 4(e) depicts histogram plot showing average lateral area of nanosheets, in accordance with an implementation of the present subject matter.

[00013] Figs. 5(a) and 5(b) depict Atomic Force Microscope (AFM) images of nanosheets obtained by using the method, in accordance with an implementation of the present subject matter.

[00014] Fig. 5(c) depicts histogram plot showing average thickness of nanosheets, in accordance with an implementation of the present subject matter.

[00015] Figs. 6(a) and 6(b) depict SEM images of nanosheets obtained by conventional probe sonication method, in accordance with an implementation of the present subject matter.

[00016] Figs. 7(a) and 7(b) depict SEM images of nanosheets obtained by conventional laser exposure, in accordance with an implementation of the present subject matter.

[00017] Figs. 8(a) and 8(b) depict the SEM image and area histogram of SEM image, respectively, obtained from sequential laser exfoliation followed by probe sonication, in accordance with an implementation of the present subject matter.

[00018] Fig. 9(a) depicts SEM image of nanosheets after a first cycle of exfoliation, in accordance with an implementation of the present subject matter.

[00019] Fig. 9(b) depicts histogram of nanosheet area, in accordance with an implementation of the present subject matter.

[00020] Fig. 9(c) depicts AFM image of nanosheets after a first cycle of exfoliation, in accordance with an implementation of the present subject matter.

[00021] Fig. 9(d) depicts nanosheet thickness, in accordance with an implementation of the present subject matter.

[00022] Fig. 10(a) depicts SEM image of nanosheets after a second cycle of exfoliation, in accordance with an implementation of the present subject matter.

[00023] Fig. 10(b) depicts histogram of area, in accordance with an implementation of the present subject matter.

[00024] Fig. 10(c) depicts AFM image of nanosheets after a second cycle of exfoliation, in accordance with an implementation of the present subject matter.

[00025] Fig. 10(d) depicts nanosheet thickness, in accordance with an implementation of the present subject matter.

[00026] Fig. 11(a) depicts SEM image of nanosheets after a third cycle of exfoliation, in accordance with an implementation of the present subject matter.

[00027] Fig. 11(b) depicts histogram of area, in accordance with an implementation of the present subject matter.

[00028] Fig. 11(c) depicts AFM image of nanosheets after a third cycle of exfoliation, in accordance with an implementation of the present subject matter.

[00029] Fig. 11(d) depicts nanosheet thickness, in accordance with an implementation of the present subject matter.

[00030] Fig. 12(a) depicts SEM image of nanosheets after a fourth cycle of exfoliation, in accordance with an implementation of the present subject matter.

[00031] Fig. 12(b) depicts histogram of area, in accordance with an implementation of the present subject matter.

[00032] Fig. 12(c) depicts AFM image of nanosheets after a fourth cycle of exfoliation, in accordance with an implementation of the present subject matter.

[00033] Fig. 12(d) depicts nanosheet thickness, in accordance with an implementation of the present subject matter.

[00034] Fig. 13(a) depicts SEM image of nanosheets after a fifth cycle of exfoliation, in accordance with an implementation of the present subject matter.

[00035] Fig. 13(b) depicts histogram of area, in accordance with an implementation of the present subject matter.

[00036] Fig. 13(c) depicts AFM image of nanosheets after a fifth cycle of exfoliation, in accordance with an implementation of the present subject matter.

[00037] Fig. 13(d) depicts nanosheet thickness, in accordance with an implementation of the present subject matter.

[00038] Fig. 14 depicts a graph illustrating variation of nanosheet sheet yield as a function of laser energy, in accordance with an implementation of the present subject matter.

[00039] Fig. 15 depicts SEM images of nanosheets of graphene, in accordance with an implementation of the present subject matter.

[00040] Fig. 16 depicts SEM images of nanosheets of MoS_2, in accordance with an implementation of the present subject matter.

[00041] Fig. 17 depicts SEM images of graphene oxide, in accordance with an implementation of the present subject matter.

DETAILED DESCRIPTION

[00042] The present subject matter provides for opto-mechanical based production of nanosheets of layered materials. While the present subject matter is explained with reference to boron nitride as an example, it is to be understood that any other layered bulk material known in the art may be produced using the techniques disclosed herein.

[00043] Generally, two-dimensional (2D) nanosheets provide enhanced functionality compared to their bulk counterparts. Commercialization of graphene-based nanosheets has been achieved today due to the success in large scale production of graphene nanosheets. Graphene-based nanosheets are currently commercially produced in

restricted forms. For example, currently available layered graphene nanosheets have a few layers of graphene sheets, or they are available as reduced graphene oxide (r-GO), and so on. Similar to graphene, there are other layered materials which in their nanosheet form can have applications in several fields. One such material is boron nitride.

[00044] Bulk hexagonal boron nitride (h-BN) is known for its applications as an insulator, ultraviolet (UV) emitter, filler in polymers for their enhanced mechanical strength and thermal conductivity, and the like. Further, nanosheets of h-BN have been reported to show enhanced functionality compared to their bulk counterparts. However, unlike graphene, large scale production of boron nitride, and other nanosheets, has remained a challenge due to its low yield.

[00045] Conventional liquid phase exfoliation methods for production of nanosheets of layered bulk material may use either of two techniques, namely, exfoliation through ultrasonication or exfoliation through laser exposure of bulk materials. In exfoliation through ultrasonication, layered bulk material is mixed in a solvent and is subjected to cavitation generated by ultrasonic waves from a probe or bath sonicator. Exfoliation through ultrasonication provides structurally and physically pure form of nanosheets. In exfoliation through laser exposure, the layered bulk material is immersed in a solvent and is exposed to pulsated or continuous laser beam. On exposure to the laser beam, the layered bulk material is exfoliated either by thermal expansion or by ablation caused by photon bombardment.

[00046] Previous reports on both ultrasonication and laser exposure have discussed quality of the exfoliation but are not forthcoming about yield efficiency. Also, the process of exfoliation may involve the use of stabilizers which may compromise the quality of nanosheets. Further, the solvent used in these two techniques are generally not environment friendly. Further, the maximum yield of nanosheets using water as solvent is lesser than 5 weight percent or dispersion concentration of 0.05 to 0.1 mg/ml.

Also, most of the research reported provide for ultrasonication for numerous hours and, therefore, is time consuming.

[00047] The present subject matter addresses these and other problems in conventional methods for production of two dimensional nanosheets from three-dimensional layered bulk materials and provides an opto-mechanical method for production of nanosheets from three-dimensional layered bulk material. A layered bulk material is contacted with a solvent to obtain a first mixture. The solvent may be selected from an aqueous solvent and a non-aqueous solvent.

[00048] The first mixture is simultaneously exposed to high energy density photons and mechanical shearing to obtain a first dispersion comprising residual bulk material, nanosheets, and the solvent. The energy of the high energy density photons used is selected based on the layered bulk material used. The high energy density photons may be provided by laser illumination and the mechanical shearing may be performed by one of: ultrasonication and shear mixing.

[00049] A first supernatant and a first residue are obtained, for example by centrifugation, from the first dispersion. The nanosheets, typically, separate into the supernatant while the residual bulk material remains in the first residue. The nanosheets can be obtained from the first supernatant by separating the nanosheets from the first supernatant, for example, by filtering the first supernatant.

[00050] In one example, the first residue may be further contacted with the solvent to obtain a second dispersion. A second supernatant and a second residue can be obtained from the second dispersion where the second supernatant comprises the nanosheets. The second residue can also be contacted with solvent to obtain a third dispersion and, corresponding third supernatant and third residue where the third supernatant comprises the nanosheets. The third supernatant can further be contacted with solvent and the process may be repeated to obtain subsequent dispersions, supernatants, and residues.

[00051] In an example, the first supernatant, the second supernatant, and subsequently formed supernatants may be mixed together for batch separation of nanosheets. In another example, any of the first residue, second residue, and so on, or their mixtures may be used as starting material, i.e., the layered bulk material as explained previously for a subsequent cycle of production of the nanosheets.

[00052] The present subject matter helps in achieving high yield of nanosheets. The method also allows for production of nanosheets at a much faster rate in comparison to conventional exfoliation. The method is scalable to large scale production. The method can easily be adapted to other layered materials.

[00053] The above and other features, aspects, and advantages of the subject matter will be better explained with regard to the following description and accompanying figures. It should be noted that the description and figures merely illustrate the principles of the present subject matter along with examples described herein and, should not be construed as a limitation to the present subject matter. It is thus understood that various arrangements may be devised that, although not explicitly described or shown herein, embody the principles of the present disclosure. Moreover, all statements herein reciting principles, aspects, and examples thereof, are intended to encompass equivalents thereof. Further, for the sake of simplicity, and without limitation, the same numbers are used throughout the drawings to reference like features and components.

[00054] Fig. 1(a) depicts an example method 100 for production of nanosheets from layered bulk material, in accordance with an implementation of the present subject matter. At block 102, the method 100 comprises contacting the layered bulk material with a solvent to obtain a first mixture.

[00055] In one example, the solvent is a non-aqueous solvent selected from the group consisting of: ethanol, N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMA), N-methyl-2-pyrolidone (NMP), and combinations thereof. High yield of nanosheets may be achieved by using strong polar solvents, such as N, N-

dimethylformamide (DMF), N, N-dimethylacetamide (DMA), N-methyl-2-pyrolidone (NMP), and the like. In some scenarios the polar solvents may be unsuitable for scalability because of their toxicity. In another example, the solvent may be an aqueous solvent, for example, water. The solvent may also be a solution of a polar solvent in water. The polar solvents may be ethanol, N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMA), N-methyl-2-pyrolidone (NMP), and combinations thereof.

[00056] In one example, the layered bulk material may be selected from the group consisting of: boron nitride, graphite, and molybdenum sulphide. In another example, the layered bulk material may be selected from the group consisting of: transition metal dichalcogenides (TMDCs), chalcogenide compounds, and borocarbonitrides. The concentration of the layered bulk material in the first mixture may be in a range of 2 mg/mL – 33 mg/mL. In one example, prior to contacting with the solvent, the layered bulk material may be subjected to pre-processing steps, such as hydro thermal reaction, oxidation, degassing, centrifugation, autoclaving, cold or heat treatment, and the like. The pre-processing step may depend on the layered bulk material used.

[00057] At block 104, the method 100 comprises simultaneously exposing the first mixture to high energy density photons and mechanical shearing to obtain a first dispersion. The first dispersion can comprise the nanosheets, residual bulk material, and the solvent. The high energy density photons may be provided, in one example, by laser illumination from a light source and the mechanical shearing may be performed by one of: ultrasonication and shear mixing. Energy of the high energy density photons used may be based on the layered bulk material used. For example, when the bulk material is boron nitride, the energy of high energy density photons may be in a range of 5 – 40 mJ and preferably in a range of 10 – 20 mJ. In an example, the simultaneous exposure to high energy density photons and mechanical shearing can be performed for 1.5 – 2 hours at a temperature in a range of 30 - 70 degree Celsius.

[00058] In one example, high energy density photons may be provided by pulsed laser illumination, for example, a nano second to a femto second pulsed laser system may be used to provide the high energy density photons.

[00059] In one example, the mechanical shearing may be performed using an ultrasonic probe sonication system. In said example, a frequency of ultrasonication may be in a range of 20 to 40 kHz and amplitude is in a range of ~ 50% to 100% of a maximum amplitude value of the probe.

[00060] At block 106, the method 100 comprises obtaining a first supernatant and a first residue from the first dispersion. The first supernatant and the first residue may be obtained, for example, by centrifugation. The first supernatant comprises the nanosheets. In one example, the centrifugation may be performed at 5000 – 7000 rpm for a time period in a range of 15 minutes to 1 hour.

[00061] At block 108, the method 100 comprises obtaining the nanosheets from the first supernatant by separating the nanosheets from the first supernatant. The nanosheets may be obtained from the first supernatant, for example, by filtration using a membrane filter. The obtained nanosheets may be further processed, for example, the nanosheets may be subjected to drying. In one example, to improve yield, the first residue may be subjected to further processing.

[00062] Fig. 1(b) depicts an extended method of production of nanosheets by further processing of the first residue, in accordance with an implementation of the present subject matter. At block 110, the method 100 comprises contacting the first residue with the solvent to obtain a second dispersion. The first residue may be contacted with the solvent in a volume ratio in a range of 1:1 – 1:12. In one example, volume ratio of first residue to solvent is 1:4. At block 112, the method 100 comprises obtaining a second supernatant and a second residue from the second dispersion. In one example, the second supernatant and the second residue may be obtained by centrifugation at 5000 – 7000 rpm. The second supernatant comprises the nanosheets. In one example, the nanosheets may be obtained from the second supernatant, for example, by filtration,

for example by membrane filtration. In another example, the second supernatant may be contacted with the first supernatant to obtain a batch of supernatants and the nanosheets can be separated from the batch of supernatants.

[00063] At block 114, the method 100 comprises contacting the second residue with the solvent to obtain a third dispersion. The second residue may be contacted with the solvent with volume ratio in a range of 1:1 – 1:12. In one example, volume ratio of the second residue to the solvent is 1:4. At block 116, the method 100 comprises obtaining a third supernatant and a third residue from the third dispersion. In one example, the third supernatant and the third residue may be obtained by centrifugation at 5000 – 7000 rpm. The third supernatant comprises the nanosheets. In one example, the nanosheets may be obtained from the third supernatant, for example, by filtration. In another example, the third supernatant may be contacted with the first and second supernatant to obtain a batch of supernatants and the nanosheets can be separated from the batch.

[00064] In one example, the third residue may be contacted with the solvent to obtain a second mixture. The second mixture may be then processed in a manner similar to the first mixture by being subjected to simultaneous exposure to high energy density photons and mechanical shearing, separation of resultant supernatant, and separation of nanosheets from the resultant supernatant in multiple steps. Such processing may be continued cyclically 'n' number of times. In one example, the cycle is repeated 5 times for one batch of layered bulk material. Residue at the end of the cycle may be discarded or may be mixed with a fresh batch of layered bulk material and then processed.

[00065] Fig. 1(c) illustrates a schematic of a method 120 for production of nanosheets from layered bulk material, in accordance with an implementation of the present subject matter. While Fig. 1(c) has been explained with hexagonal boron nitride (h-BN) as a bulk material, it is to be understood that other layered material may be used instead of or in addition to h-BN.

[00066] At block 122, a batch of layered bulk material, for example, as shown in Fig. 1(c), h-BN is obtained. In one example, PT110 grade of h-BN was used. However, other grades may also be used. At block 124, the layered bulk material is mixed with the solvent to obtain the first mixture. The first mixture, therefore, comprises the layered bulk material in the solvent. The first mixture is then simultaneously exposed to high energy density photons and mechanical shearing, for example, by laser illumination and ultrasonication, at block 126, to obtain a first dispersion 125a. In one example, frequency of sonication is in a range of 20 to 40 kHz and amplitude is in a range of ~ 50% to 100%. In an example, an ultrasonic probe sonication system is used for sonication. In one example, pulsed laser frequency is in a range of 5 to 10 Hz. The first dispersion 125a comprises the nanosheets, residual bulk material, and solvent. The first dispersion 125a can be centrifuged, at block 128a, to separate a first supernatant 127a from a first residue 129a. The nanosheets remain predominantly in the first supernatant 127a while residual bulk material along with residual nanosheets remains in the first residue 129a.

[00067] In an example, the first supernatant 127a is then filtered to obtain the nanosheets. However, to increase efficiency of production, in another example, the first residue 129a can be subjected to further processing. The first residue 129a may be mixed with the solvent to obtain a second dispersion 125b for further processing.

[00068] As shown in Fig. 1(c), at block 128b, the second dispersion 125b can be centrifuged to obtain a second supernatant 127b and a second residue 129b. The second residue 129b obtained can again be mixed with the solvent to obtain a third dispersion 125c. At block 128c, centrifugation can be repeated with reference to the third dispersion 125c to obtain a third residue 129c and a third supernatant 127c. For purpose of illustration, Fig. 1(c) depicts three rounds of centrifugation, i.e., at block 128a, 128b, 128c. However, a greater number of rounds of centrifugation can be performed in other examples as will be understood.

[00069] In an example, to obtain the second dispersion 125b and third dispersion 125c, the first residue 129a and second residue 129b can be mixed with the solvent with solvent in a volume ratio in a range of 1:1 – 1:12, preferably in a volume ratio of 1:4. At block 128b and 128c, the second dispersion 125b and third dispersion 125c can be centrifuged for about an hour at 5000 rpm to obtain the second supernatant 127b and the second residue 129b; and third supernatant 127c and the third residue 129c, respectively.

[00070] Supernatants from centrifugation at block 128a, 128b, 128c, i.e., first supernatant 127a, second supernatant 127b, third supernatant 127c, and so on, can be collected. At block 130, collected supernatant can be subjected to filtration, for example, membrane filtration, vacuum filtration, and the like, to obtain the nanosheets in powder form.

[00071] In an example, residue obtained at an end of block 129c, i.e., after centrifugations can be used as the bulk material at block 122. In an example, the residue can be mixed with a fresh solvent for repetition of cycle blocks 124 – 130.

[00072] By simultaneously exposing the mixture to high energy density photons and mechanical shearing, there is simultaneous cavitation and photon bombardment. This helps in facilitating and accelerating exfoliation and separating individual layers from the bulk material more efficiently than conventional techniques.

[00073] Fig. 2 illustrates an assembly 200 for production of the nanosheets, in accordance with an implementation of the present subject matter. The assembly 200 can comprise an enclosure 201 to in which the nanosheets may be produced. A mixture of layered bulk material and solvent, such as the first mixture, second mixture, etc., may be held in a vessel, such as vessel 202. The vessel 202 can be placed in the enclosure 201. The vessel 202 may be integrally formed with or detachable from the enclosure 201.

[00074] The assembly 200 can also comprise a light source 204 for providing high energy density photons. The vessel 202 holding the mixture of the layered bulk material

is placed in the optical path of the high energy density photons produced by the light source 204. In an example, the light source 204 is a nano second to a femto second pulsed laser system. In an example, the light source 204 is a neodymium-doped yttrium aluminium garnet (Nd:YAG) based system. The assembly 200 can also comprise an ultrasonic probe sonication system comprising a probe 206 which can be placed in the mixture for sonication of the mixture. The mixture can be simultaneously exposed to high energy density photons and sonication to obtain the nanosheets.

[00075] As is known, during simultaneous exposure to high energy density photons and sonication, temperature of the mixture may increase. Thus, during simultaneous exposure, the mixture may have to be cooled to maintain the temperature in the range of 30 – 70 degree Celsius. The enclosure 201 can, thus, hold a cooling material to cool the mixture. The cooling material may be in contact with at least a portion of the external surface of the vessel 202.

[00076] To prevent the cooling material from interfering with the optical path of the high energy density photons, the enclosure 201 can have a first portion 201a and a second portion 201b which are separated. The second portion 201b may face the optical path of the high energy density photons. In one example, the first portion 201a and the second portion 201b may be separated by a chamber 201c. In said example, the chamber 201c may also form the second portion 201b.

[00077] The first portion 201a can contain the cooling material to cool the mixture during simultaneous exposure to high energy density photons and sonication. The cooling material may be ice which has been deposited in the first portion 201a. However, other cooling material, such as ice pack, circulating coolant, and the like, may also be used. To prevent interference with the optical path of the high energy density photons, the second portion 201b may not contain the cooling material. In one example, the second portion 201b may contain small amounts of the cooling material placed so as to not interfere with the optical path of the high energy density photons. The chamber 201c (boundary of which is indicated by the dotted lines) may be formed

in the second portion 210b to ensure that the cooling material does not interference with the optical path of the high energy density photons. The chamber 201c may be kept empty and may act as partition which separates the first portion 201a from the second portion 201b. As the second portion 201b may not contain or may only partially be filled with the cooling material, the high energy density photons can be received by the mixture through the second portion 201b of the enclosure 201 without any interference.

[00078] For mechanical shearing, the ultrasonic probe sonication system can comprise the probe 206 connected to an ultrasonic generator 208. The probe 206 can be immersed in the mixture for sonication. In an example, the ultrasonic generator 208 can be operated at 60% of maximum amplitude at 3 s on and off cycles. The vessel 202 can be placed in the enclosure 201 so that the light source 204 can provide high energy density photons at 1 – 2 cm below the probe 206.

[00079] In an example, the light source 204 can provide a pulsed laser of 532 nm with a pulse duration of 6 ns at a frequency of 10 Hz. However, the wavelength and pulse duration provided can be varied depending on the layered bulk material to be exfoliated. Both the light source 204 and the ultrasonic generator 208 can be switched on simultaneously to carry out exfoliation of the bulk material for about 2 hrs. By simultaneously exposing the mixture to mechanical shearing via sonication and high energy density photons, for example, by laser illumination, there is simultaneous cavitation and photon bombardment which facilitates in accelerating production of nanosheets and provides higher yield.

[00080] In some examples, high yield of nanosheets may be obtained using water as solvent, thereby allowing for production of nanosheets without organic solvents and making the process more environmentally friendly and scalable.

[00081] Fig. 3(a) depicts a schematic representation of exfoliation of bulk boron nitride, in accordance with an implementation of the present subject matter. For ease of representation, the solvent is not depicted. Rather only the material being exfoliated

is depicted in Fig. 3(a). The bulk material represented by 301 in the mixture is subjected to exfoliation by simultaneously exposing it to high energy density photons and mechanical shearing for 2 hours, in step 302, forming a dispersion comprising individual or few layers of the nanosheets shown as 303. Therefore, the dispersion can comprise flakes of all sizes. To separate the nanosheets based on their size, the dispersion is subjected to centrifugation at step 304. Repeated washing, where each wash may include centrifugation as shown in block 128a, 128b, 128c of Fig. 1(c), helps in collection and more efficient separation of the nanosheets 306. In an example, yield of nanosheets 306 obtained using the example method of the present subject matter is greater than 40% (by weight) and the obtained nanosheets have a thickness in a range of 4 – 15 nm with an average lateral size of 0.5 to 1 μm^2.

[00082] Fig. 3(b) depicts Scanning Electron Microscope (SEM) image of bulk material, in accordance with an implementation of the present subject matter. Fig. 3(c) depicts SEM image of layered nanosheets obtained by using the method of the present subject matter, in accordance with an implementation of the present subject matter.

[00083] The present subject matter will now be illustrated with working examples, which are intended to illustrate the working of disclosure and not intended to be taken restrictively to imply any limitations on the scope of the present disclosure. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this disclosure belongs. It is to be understood that this disclosure is not limited to the particular methods and experimental conditions described, as such methods and conditions may vary depending on the process and inputs used as will be easily understood by a person skilled in the art.

EXAMPLES

EXAMPLE 1: COMPARATIVE STUDY

[00084] In this example, efficiency of the present method in terms of nanosheet yield (in wt.% of the bulk material) was compared with other conventional methods. Like in the present method of exfoliation, h-BN was also exfoliated by three other individual techniques, namely, 'exfoliation by probe sonication', 'exfoliation by laser exposure' and 'exfoliation by laser exposure followed by probe sonication'. In the above cases, the probe sonication was performed at amplitude of 60% of maximum amplitude, 3 seconds on-off cycle, and at 20 kHz; and the laser illumination used had a wavelength of 532 nm, at a frequency of 10 Hz, 6 ns pulse, and laser energy of 15 mJ. Yield was compared at two different rotation per minute (rpm) of centrifugation. As a trial, the mixture was also subjected to centrifugation at higher rpm instead of 5000 rpm. Centrifugation with rpm of about 7000 resulted in finer quality, fewer layers of boron nitride nanosheets with lower yield as shown in Table 1.

Table 1: Nanosheet yield comparison between different methods

Speed of Centrifugation used for separation of the nanosheets after exfoliation	Exfoliation by 2hours Simultaneous laser exposure and probe sonication (Yield in wt %)	Exfoliation by 2hours only probe sonication (Yield in wt %)	Exfoliation by 2hours only laser exposure (Yield in wt %)	Exfoliation by 2hours laser exposure followed by 2 hours probe sonication (Yield in wt %)
5000 rpm	12.065	5.124	6.99	7.9775
7000 rpm	2.49	1.281	1.2	1.3975

[00085] Fig. 4(a) depicts SEM image of layered nanosheets obtained at 5000 rpm for centrifugation. Fig(s). 4(b), (c) and (d) depict SEM images of layered nanosheets

obtained at 7000 rpm for centrifugation. From the SEM images as shown in Fig. 4(a), 4(b), 4(c), and 4(d), it was observed that layered nanosheets of lesser thickness were obtained using 7000 rpm as compared to 5000 rpm. The thickness was observed to be in a range of 3 nm – 20 nm. The method of the present subject matter as shown in Fig. 1(a) was used to obtain the layered nanosheets as shown in Fig(s). 4(a)-(d). Fig. 4(e) depicts histogram plot of count with respect to area of the layered nanosheets obtained from the SEM images shown in Fig. 4(a) – (d) and other similar images. The histogram showed that majority of the layered nanosheets had area in a range of 0.5-3 μm^2.

[00086] Fig. 5(a) depicts Atomic Force Microscopy (AFM) images of layered nanosheets obtained at 5000 rpm for centrifugation. Fig. 5(b) depicts AFM image of layered nanosheets obtained at 7000 rpm for centrifugation. Fig. 5(c) depicts histogram plot of count with respect to thickness of the layered nanosheets obtained from AFM images as shown in Fig. 5(a) and 5(b) and other such AFM images. The histogram showed that majority of the layered nanosheets had thickness in a range of 4-20 nm.

[00087] Further, as shown in Table 1, comparative study was conducted with reference to yield of conventional methods for production of layered nanosheets and the method of the present subject matter.

[00088] Fig. 6(a) depicts SEM images of layered nanosheets obtained by conventional probe sonication method, in accordance with an implementation of the present subject matter. To obtain the layered nanosheets, 10 gm of h-BN powder was mixed in 300 mL of pure water. The mixture was subjected to probe sonication by using ultrasonic liquid processor from Johnson Plastosonic operated at 60% of its maximum amplitude at 20 kHz in 3 s on and off cycle. The temperature of the first dispersion was maintained at less than 50°C by immersing the vessel containing the mixture in an ice bath during sonication. Sonication was carried out for 2 hours. Resultant dispersion was repeatedly washed and subjected to centrifugation at 5000 rpm. Supernatant collected after three washes was subjected to filtration through a membrane filter. Any membrane having pore size in few hundreds of nano meter range may be used. The process was repeated

for 5 cycles of exfoliation, where one cycle of exfoliation comprised: sonication, three washes and centrifugation, and filtration through the membrane filter. Fig. 6(a) and 6(b) depict SEM images and Table 1 depicts yield.

[00089] Figs. 7(a) and 7(b) depict SEM images of layered nanosheets obtained by conventional laser exposure, in accordance with an implementation of the present subject matter. To obtain results for this, 10 gm of h-BN was dispersed in 300 mL of water and the mixture was subjected to exfoliation by exposing it to the Nd:YAG laser at 532 nm with pulse duration of 6 ns at repetition rate of 10 Hz for 2 hours. The resultant dispersion was washed as explained with reference to block 108 of Fig. 1. Supernatants were filtered to obtain the layered nanosheets. Figs. 7(a) and 7(b) depict SEM images and Table 1 depicts yield.

[00090] Sequential exposure to laser and probe sonication was also studied. 10g of h-BN was dissolved in pure water. The first dispersion so obtained was subjected to 2 hours of pulsed laser exposure while the dispersion container was kept in a bath sonicator to aid in uniform laser exposure. The Nd:YAG laser of 532 nm with pulse duration of 6 ns at a repetition rate of 10 Hz was used. Resultant mixture was subjected to probe sonication in an ultrasonicator, Johnson Plastosonic, (model ULP 500) operated at 60% of its maximum amplitude at 20 kHz with 3 seconds on and off cycle for 2 hrs. Resultant dispersion was subjected to repeated washing and centrifugation. Supernatant collected after three washes were subjected to filtration through a membrane filter. The yield was as shown in Table 1 and Figs. 8(a) and 8(b) depict the SEM image and area histogram of SEM image, respectively. It was observed that the method of the present subject matter provides higher yield compared to conventional techniques and sequential usage of conventional techniques.

EXAMPLE 2: EFFECT OF REPETITIVE EXFOLIATION CYCLES

[00091] In this example, SEM and AFM images of the layered nanosheets obtained after every cycle of exfoliation (having parameters as discussed for Example 1) are

discussed along with the nanosheet yield. A cycle of exfoliation comprises of steps as described with reference to 104-110 as shown in Fig. 1(a).

[00092] Figs. 9(a) and 9(c) depict SEM and AFM images respectively of layered nanosheets after a first cycle of exfoliation. Figs. 9(b) and 9(d) depict histogram of area and thickness of layered boron nitride nanosheets, respectively. It was observed that the layered nanosheets were agglomerated in most areas due to solvent drying.

[00093] Figs. 10(a) and 10(c) depict SEM and AFM images respectively of layered nanosheets after a second cycle of exfoliation. Fig. 10(b) and 10(d) depict histogram of area and thickness of layered boron nitride nanosheets, respectively. It was observed that the layered nanosheets were agglomerated in most areas due to solvent drying.

[00094] Figs. 11(a) and 11(c) depict SEM and AFM images respectively of layered nanosheets after a third cycle of exfoliation. Figs. 11(b) and 11(d) depict histogram of area and thickness of layered boron nitride nanosheets, respectively. It was observed that the layered nanosheets were agglomerated in most areas due to solvent drying.

[00095] Figs. 12(a) and 12(c) depict SEM and AFM images respectively of layered nanosheets after a fourth cycle of exfoliation. Figs. 12(b) and 12(d) depict histogram of area and thickness of layered boron nitride nanosheets, respectively. It was observed that the layered nanosheets were agglomerated in most areas due to solvent drying.

[00096] Figs. 13(a) and 13(c) depict SEM and AFM images respectively of layered nanosheets after a fifth cycle of exfoliation. Figs. 13(b) and 13(d) depict histogram of area and thickness of layered boron nitride nanosheets, respectively. It was observed that the layered nanosheets were agglomerated in most areas due to solvent drying.

[00097] Table 2 depicts yield (in wt.%) of layered boron nitride nanosheets obtained in each cycle of exfoliation using the method of the present subject matter (i.e. simultaneous laser exposure and probe sonication) in comparison to only probe sonication. It was observed that the method of the present subject matter provided higher yield than only probe sonication.

Table 2: Study of effect of number of exfoliation cycles (yield in weight %)

No of cycles of exfoliation→ Method↓	1 (yield wt%)	2 (yield wt%)	3 (yield wt%)	4 (yield wt%)	5 (yield wt%)	Total yield (wt%)
Simultaneous laser exposure and probe sonication	13.8	10.4	9.7	6.2	4.06	44.16
Only probe sonication	3.4	5.1	3.4	5.8	4	21.7

EXAMPLE 3: OPTIMIZATION OF LASER ENERGY

[00098] In this example, the effect of laser energy provided by the laser system on yield of nanosheets was studied. An Nd-YAG laser system which produces a pulsed laser illumination of 532 nm with pulse duration of 6 ns at a repetition rate of 10 Hz was used for laser exfoliation. The laser energy was varied to understand its effect on layered material exfoliation.

[00099] In the process of simultaneous laser illumination and ultrasonication, the absence of laser illumination was considered as the zero-laser energy point. Similarly, the exfoliation was carried out at different energies, 10 mJ (millijoule), 15 mJ, 20 mJ, 30 mJ and 40 mJ. All these individual exfoliation processes were analyzed for nanosheet yield and quality.

[000100] Fig. 14 depicts a graph illustrating variation of nanosheet sheet yield as a function of laser energy, in accordance with an implementation of the present subject

matter. It was observed that the yield of nanosheets is significantly higher for simultaneous laser illumination along with ultrasonication when compared to only ultrasonication (zero laser energy). It was also observed that, the laser energy in a range of 13 - 15 mJ was effective in increasing the yield of boron nitride nanosheets.

EXAMPLE 4: PRODUCTION OF NANOSHEETS OF GRAPHENE, MOLYBDENUM DISULPHIDE, AND GRAPHENE OXIDE

[000101] Using the method of the present subject matter, nanosheets of graphene, MoS_2 and graphene oxide (GO) were prepared. Fig(s). 15 to 17 show SEM images of exfoliated nanosheets of graphene, MoS_2 and GO, respectively. To obtain graphene nanosheets, probe sonication was performed at amplitude of 60% of maximum amplitude, 3 seconds on-off cycle, and at 20 kHz; and the laser illumination used had a wavelength of 532 nm, at a frequency of 10 Hz, 6 ns pulse, and laser energy of 20 mJ for 2 hrs. To obtain the molybdenum disulphide nanosheets, probe sonication was performed at amplitude of 60% of maximum amplitude, 3 seconds on-off cycle, and at 20 kHz; and the laser illumination used had a wavelength of 532 nm, at a frequency of 10 Hz, 6 ns pulse, and laser energy of 20 mJ for 2 hrs. To obtain the graphene oxide nanosheets, probe sonication was performed at amplitude of 60% of maximum amplitude, 3 seconds on-off cycle, and at 20 kHz; and the laser illumination used had a wavelength of 532 nm, at a frequency of 10 Hz, 6 ns pulse, and laser energy of 12 mJ for 1 hour. Centrifugation in all three cases was performed at 7000 rpm.

[000102] The method of the present subject matter allows for high yield of layered nanosheets. The method combines mechanical shear of sonication and high energy density of optical illumination to obtain the high yield of layered nanosheets. A shorter duration is required to produce the layered nanosheets using the method. Further, the method is environmentally friendly as it allows for reusing the residue from previous cycles and uses pure water as a solvent. The method is also scalable easily to industrial level.

[000103] Although the subject matter has been described in considerable detail with reference to certain examples and implementations thereof, other implementations are possible. As such, the scope of the present subject matter should not be limited to the description of the preferred examples and implementations contained therein.

5

I/ We claim:

1. A method for production of nanosheets from layered bulk material comprising:

contacting the layered bulk material with a solvent to obtain a first mixture;

simultaneously exposing the first mixture to high energy density photons and mechanical shearing to obtain a first dispersion, wherein the first dispersion comprises the nanosheets, residual bulk material, and the solvent, wherein energy of the high energy density photons used is selected based on the layered bulk material;

obtaining a first supernatant and a first residue from the first dispersion, wherein the first supernatant comprises the nanosheets; and

obtaining the nanosheets from the first supernatant by separating the nanosheets from the first supernatant.

2. The method as claimed in claim 1, wherein the solvent is selected from an aqueous solvent and a non-aqueous solvent.

3. The method as claimed in claim 2, wherein the aqueous solvent is selected from the group consisting of: water, a solution of one of: ethanol, N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMA), N-methyl-2-pyrolidone (NMP), and combination thereof, in water.

4. The method as claimed in claim 2, wherein the non-aqueous solvent is selected from the group consisting of: ethanol, N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMA), and N-methyl-2-pyrolidone (NMP).

5. The method as claimed in claim 1, wherein the layered bulk material is selected from the group consisting of: boron nitride, graphite, graphene oxide, and molybdenum sulphide.

6. The method as claimed in claim 1, wherein the layered bulk material is selected from the group consisting: transition metal dichalcogenides (TMDCs), chalcogenide compounds, and borocarbonitrides.

7. The method as claimed in claim 1, wherein the layered bulk material is boron nitride and the energy of the high energy density photons is in a range of 5 – 40 mJ.

8. The method as claimed in claim 7, wherein the energy of the high energy density photons is in a range of 10 – 20 mJ.

9. The method as claimed in claim 1, wherein concentration of the layered bulk material in the first mixture is in a range of 2 mg/mL – 33 mg/mL.

10. The method as claimed in claim 1, wherein the high energy density photons are provided by laser illumination.

11. The method as claimed in claim 1, wherein the mechanical shearing is performed by one of: ultrasonication and shear mixing.

12. The method as claimed in claim 11, wherein a frequency of ultrasonication is in a range of 20 – 40 kHz.

13. The method as claimed in claim 1, wherein the method comprises:

contacting the first residue with the solvent to obtain a second dispersion; and

obtaining a second supernatant and a second residue from the second dispersion, wherein the second supernatant comprises the nanosheets.

14. The method as claimed in claim 13, wherein a volume ratio of the first residue to the solvent in the second dispersion is in a range of 1:1 – 1:12.

15. The method as claimed in claim 13, wherein the method comprises:

contacting the second residue with the solvent to obtain a third dispersion; and

obtaining a third supernatant and a third residue from the third dispersion, wherein the third supernatant comprises the nanosheets.

16. The method as claimed in claim 15, wherein a volume ratio of the second residue to the solvent in the third dispersion is in a range of 1:1 – 1:12.

17. The method as claimed in claim 15, wherein the method comprises:

contacting the first supernatant, the second supernatant, and the third supernatant to obtain a batch of supernatants; and

obtaining the nanosheets by separating the nanosheets from the batch of supernatants.

18. The method as claimed in claim 15, wherein the method comprises:

contacting the third residue with the solvent to obtain a second mixture; and

cyclically repeating simultaneous exposure to laser illumination and sonication, separation of resultant supernatant, and separation of nanosheets from the resultant supernatant to obtain the nanosheets.

19. An assembly (200) for production of nanosheets comprising:

an enclosure (201) to hold a vessel (202) containing a mixture of layered bulk material and solvent, the enclosure comprising a first portion (201a) and a second portion (201b), wherein the first portion contains a cooling material to cool the vessel (202);

a light source (204), wherein the vessel (202) containing the mixture of layered bulk material is placed in an optical path of high energy density photons provided by the light source, wherein the high energy density photons are to pass through the second portion (201b) of the enclosure (201) and into the vessel (202) for being absorbed by the mixture; and

an ultrasonic probe sonication system comprising a probe (206) placed in the vessel (202) for sonication of the mixture, wherein the mixture is to be simultaneously exposed to high energy density photons and sonication to obtain the nanosheets.

20. The assembly (200) as claimed in claim 19, wherein the cooling material is in contact with at least a portion of the vessel (202).

21. The assembly (200) as claimed in claim 19, wherein the light source (204) is to provide laser illumination, wherein the laser illumination is to be provided 1 – 2 cm below the probe (206) of the ultrasonic probe sonication system in the vessel (202).

22. The assembly (200) as claimed in claim 19, wherein the light source (204) is a nano second to a femto second pulsed laser system.

23. The assembly (200) as claimed in claim 19, wherein the light source (204) provides a pulsed laser illumination of 532 nm with a pulse duration of 6 ns at a frequency of 10 Hz.

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24. The assembly (200) as claimed in claim 19, wherein the first portion (201a) and the second portion (201b) of the enclosure (201) are separated by a partition to prevent interference of the cooling material with the optical path of the laser illumination.

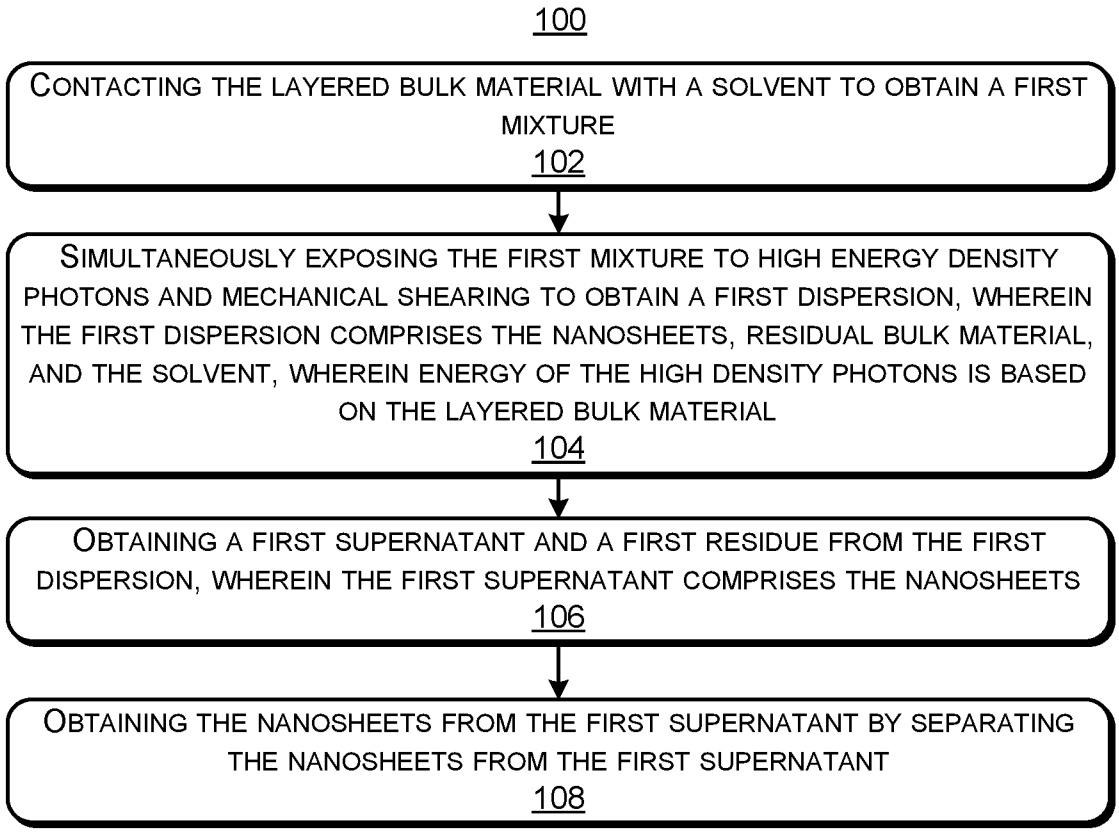
100
CONTACTING THE LAYERED BULK MATERIAL WITH A SOLVENT TO OBTAIN A FIRST MIXTURE
102
SIMULTANEOUSLY EXPOSING THE FIRST MIXTURE TO HIGH ENERGY DENSITY PHOTONS AND MECHANICAL SHEARING TO OBTAIN A FIRST DISPERSION, WHEREIN THE FIRST DISPERSION COMPRISES THE NANOSHEETS, RESIDUAL BULK MATERIAL, AND THE SOLVENT, WHEREIN ENERGY OF THE HIGH DENSITY PHOTONS IS BASED ON THE LAYERED BULK MATERIAL
104
OBTAINING A FIRST SUPERNATANT AND A FIRST RESIDUE FROM THE FIRST DISPERSION, WHEREIN THE FIRST SUPERNATANT COMPRISES THE NANOSHEETS
106
OBTAINING THE NANOSHEETS FROM THE FIRST SUPERNATANT BY SEPARATING THE NANOSHEETS FROM THE FIRST SUPERNATANT
108

Fig. 1(a)

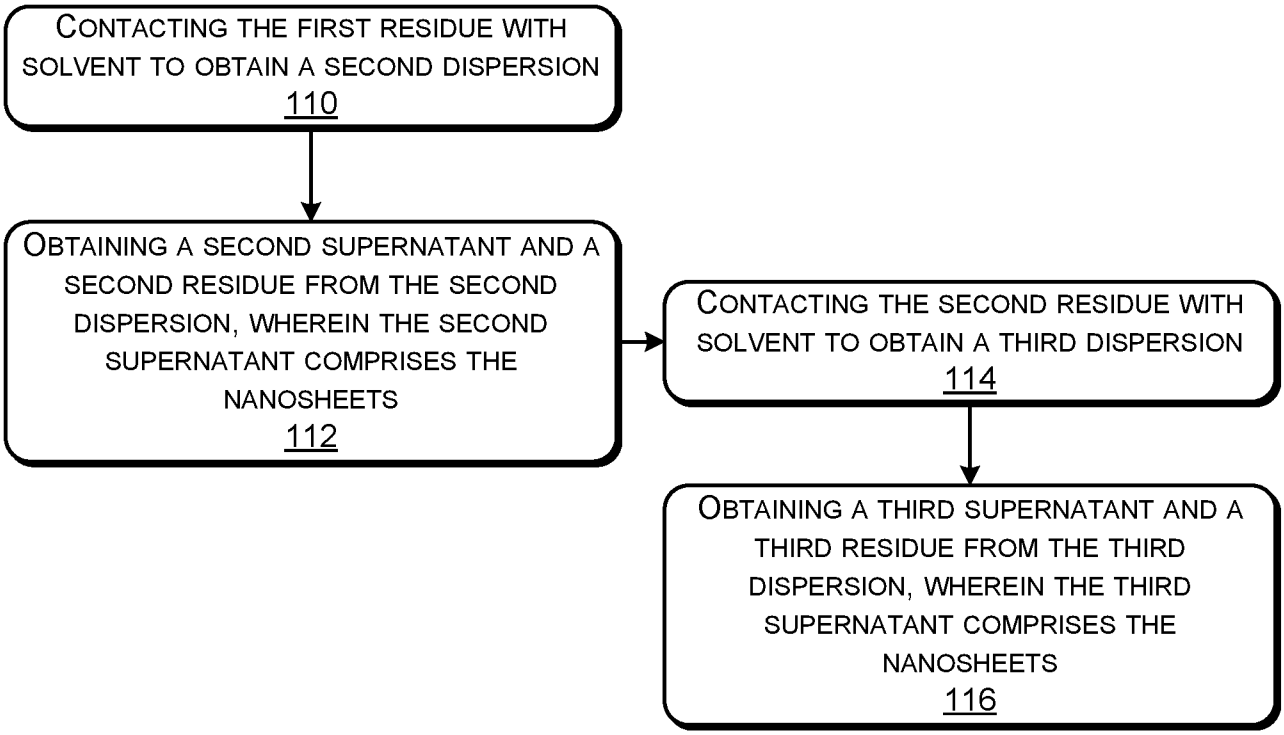
CONTACTING THE FIRST RESIDUE WITH SOLVENT TO OBTAIN A SECOND DISPERSION
110
OBTAINING A SECOND SUPERNATANT AND A SECOND RESIDUE FROM THE SECOND DISPERSION, WHEREIN THE SECOND SUPERNATANT COMPRISES THE NANOSHEETS
112
CONTACTING THE SECOND RESIDUE WITH SOLVENT TO OBTAIN A THIRD DISPERSION
114
OBTAINING A THIRD SUPERNATANT AND A THIRD RESIDUE FROM THE THIRD DISPERSION, WHEREIN THE THIRD SUPERNATANT COMPRISES THE NANOSHEETS
116

Fig. 1(b)

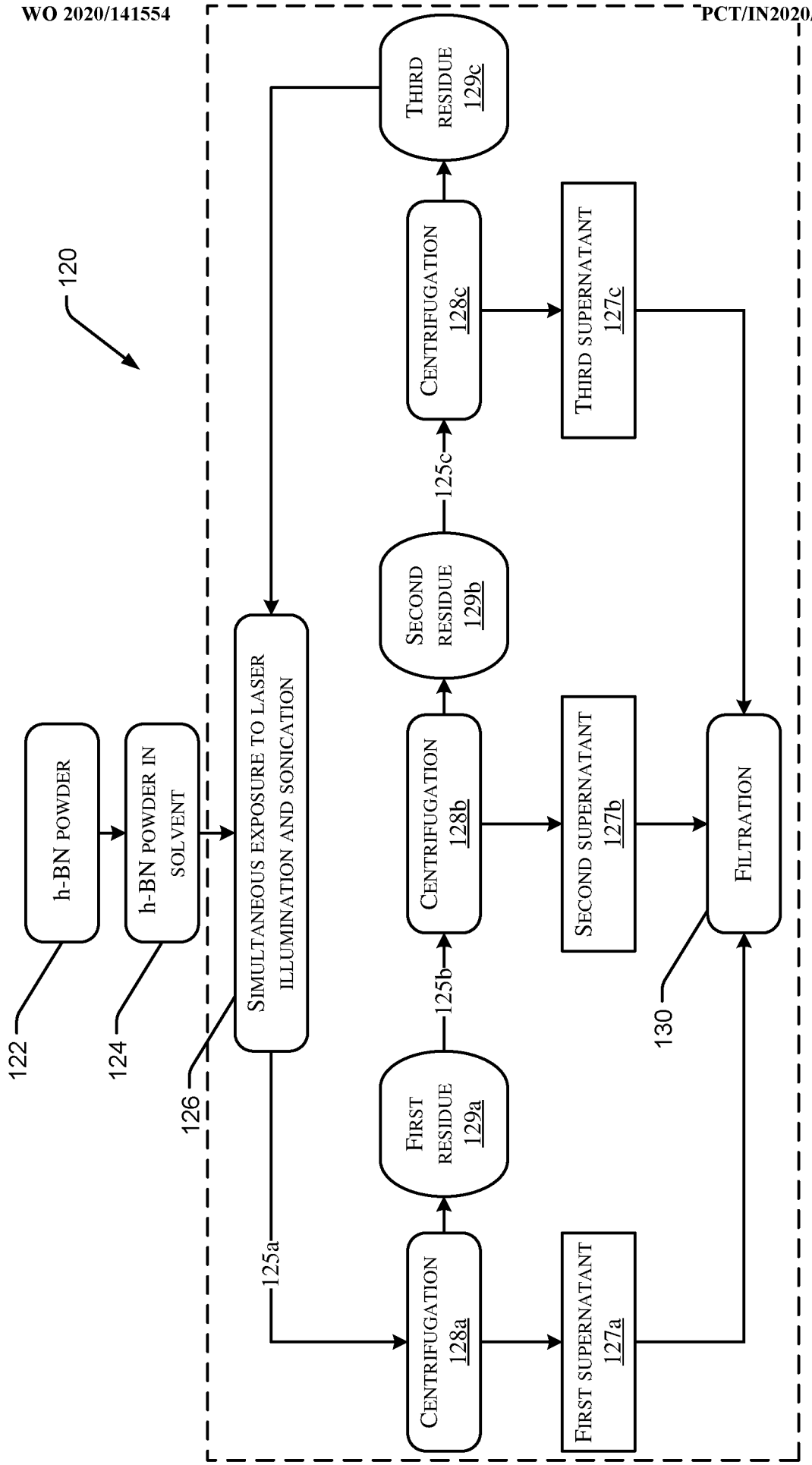
120
h-BN POWDER
122
h-BN POWDER IN SOLVENT
124
126
SIMULTANEOUS EXPOSURE TO LASER ILLUMINATION AND SONICATION
125a
CENTRIFUGATION 128a
FIRST RESIDUE 129a
125b
CENTRIFUGATION 128b
SECOND RESIDUE 129b
125c
CENTRIFUGATION 128c
THIRD RESIDUE 129c
FIRST SUPERNATANT 127a
SECOND SUPERNATANT 127b
THIRD SUPERNATANT 127c
130
FILTRATION

Fig. 1(c)

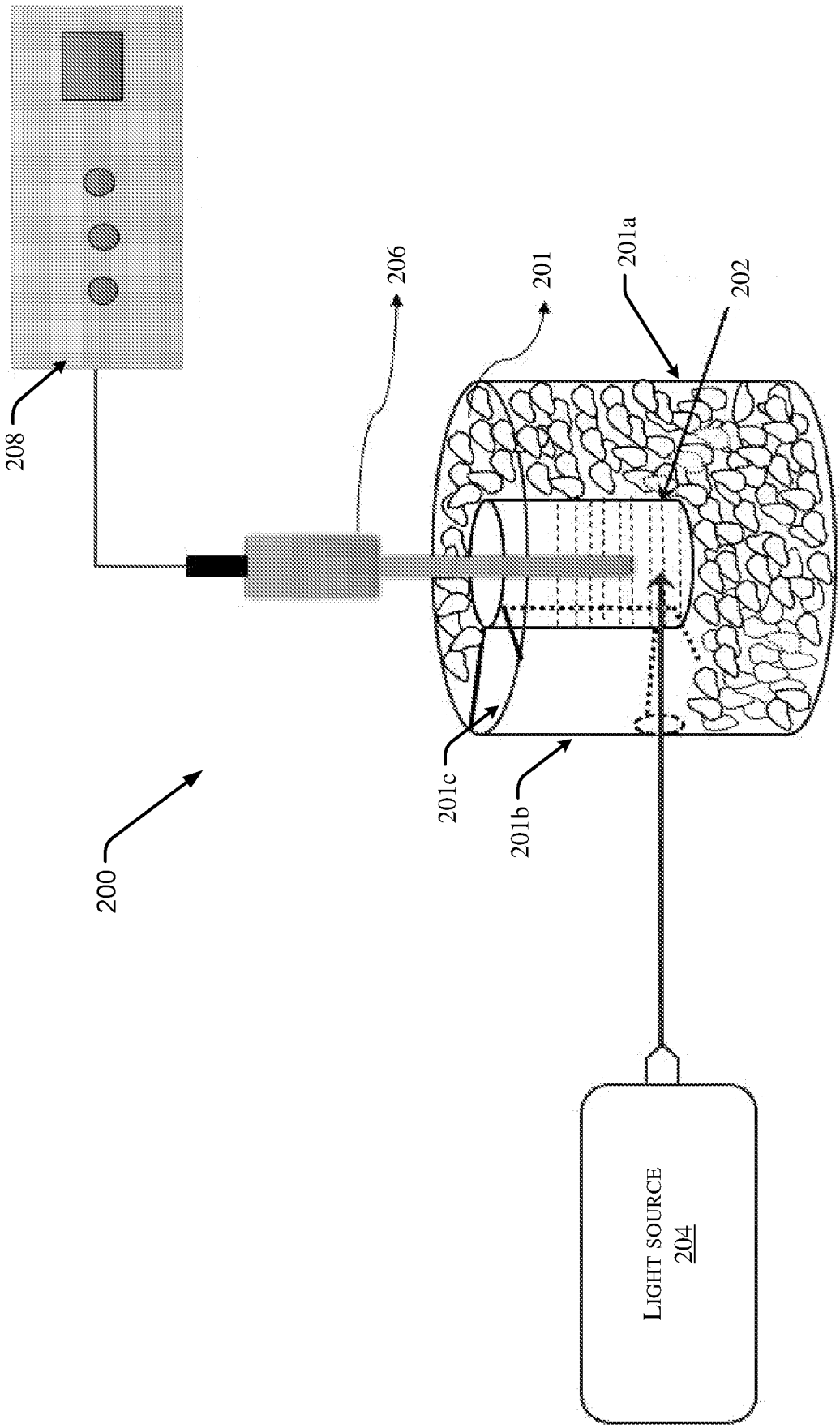

Fig. 2

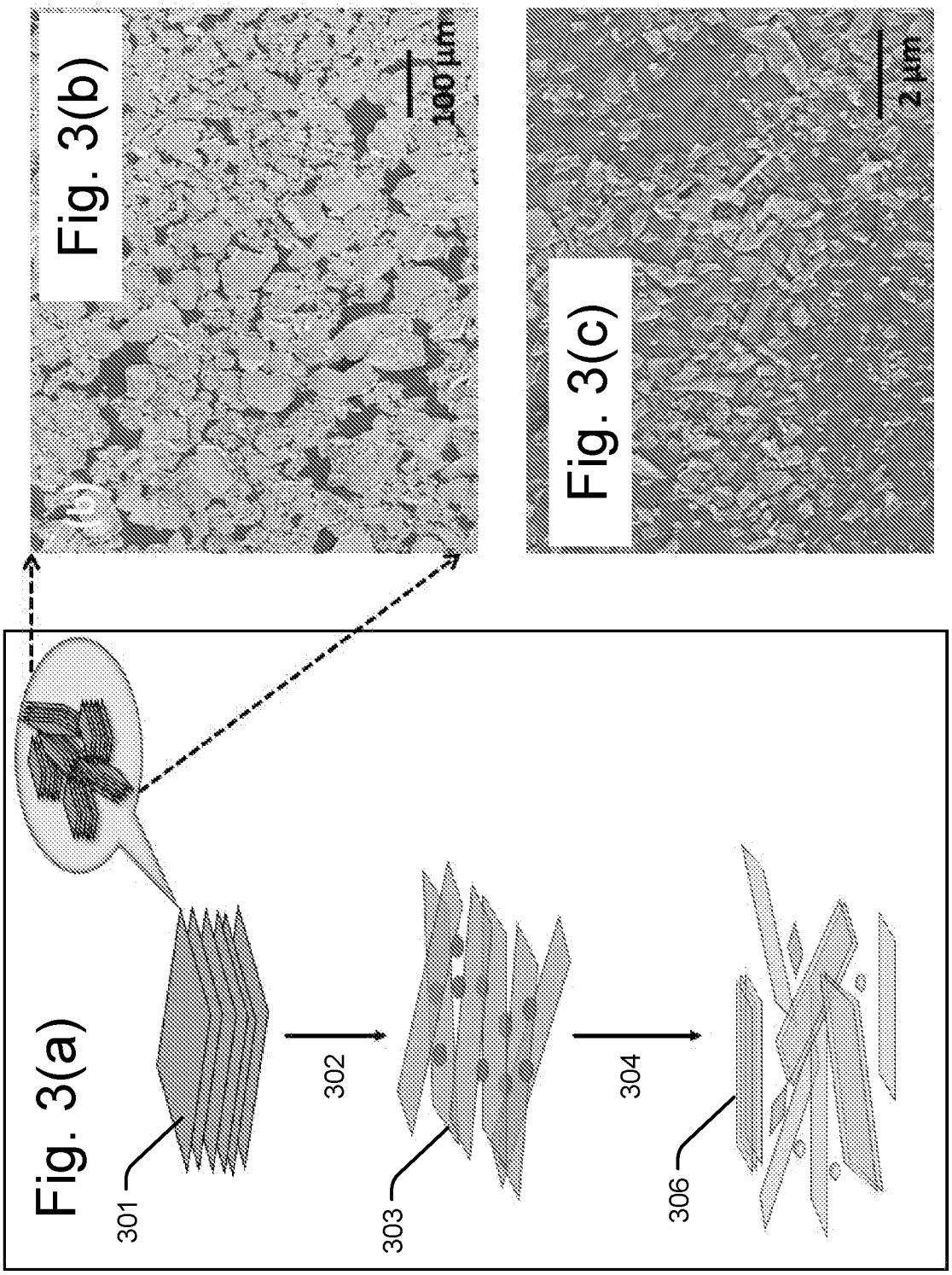
Fig. 3(a)
301
302
303
304
306
Fig. 3(b)
100 µm
Fig. 3(c)
2 µm

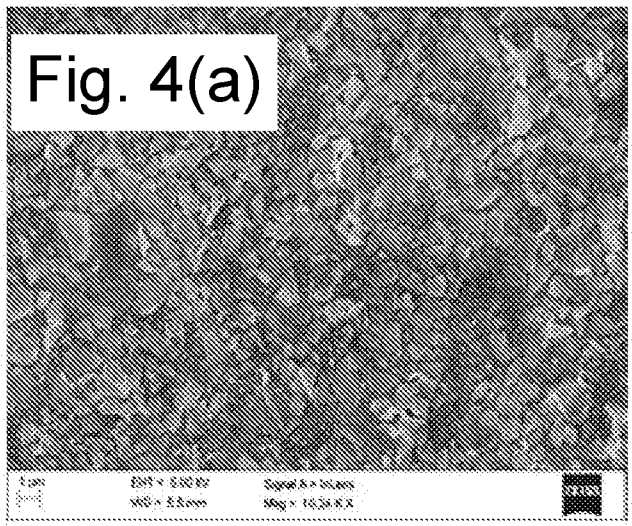
Fig. 4(a)

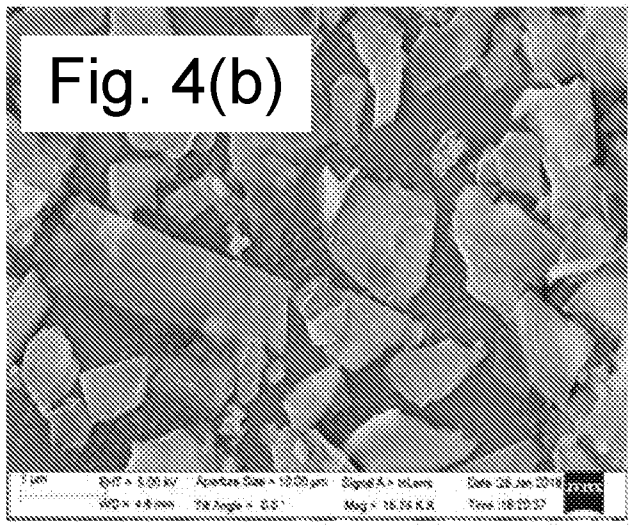
Fig. 4(b)

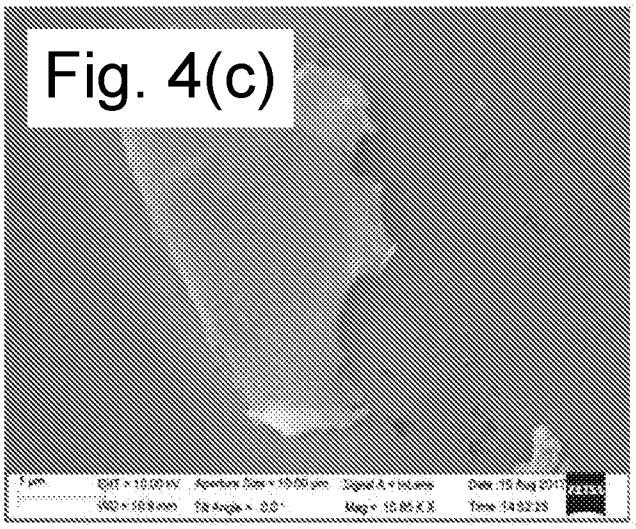
Fig. 4(c)

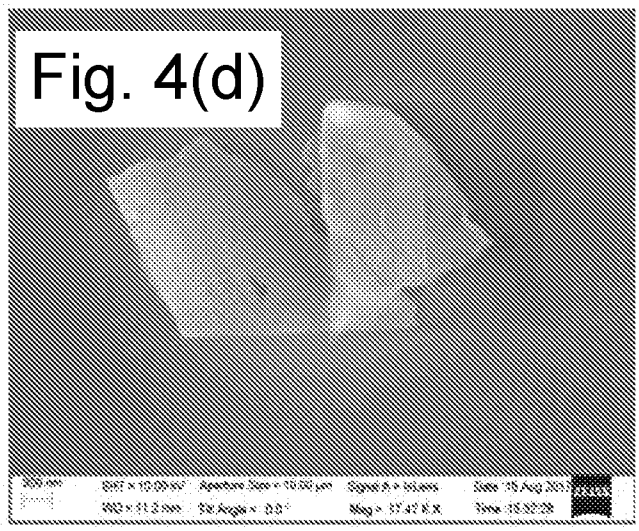
Fig. 4(d)

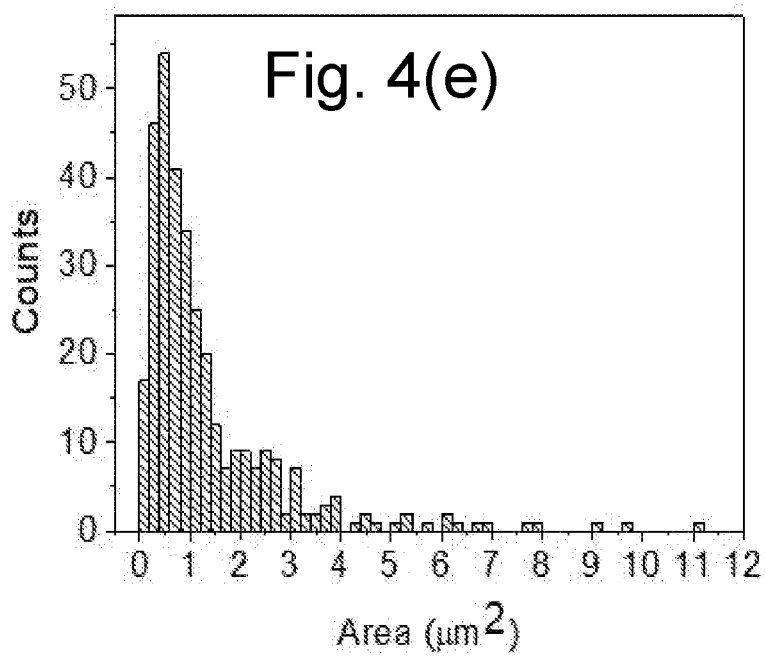
Fig. 4(e)
Counts
0
10
20
30
40
50
0 1 2 3 4 5 6 7 8 9 10 11 12
Area (μm2)

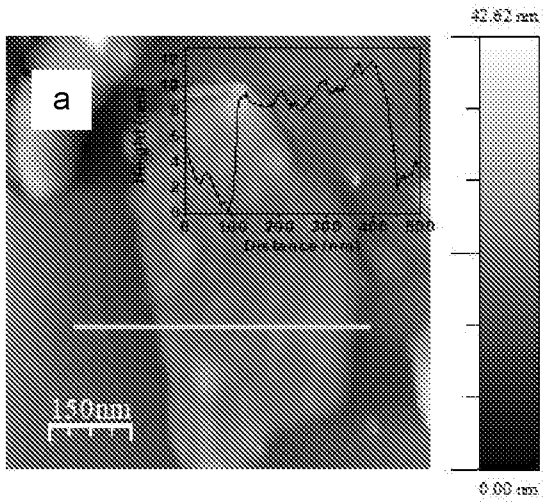

Fig. 5(a)

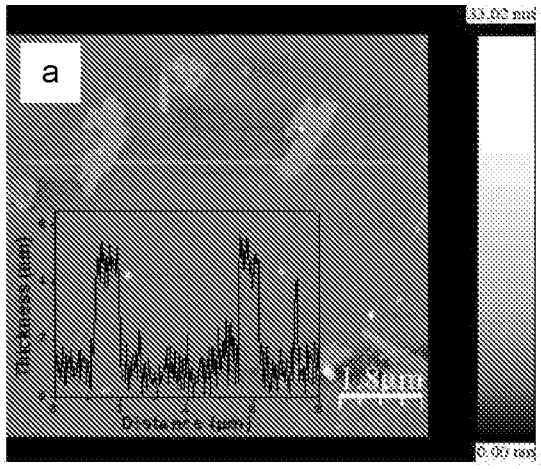

Fig. 5(b)

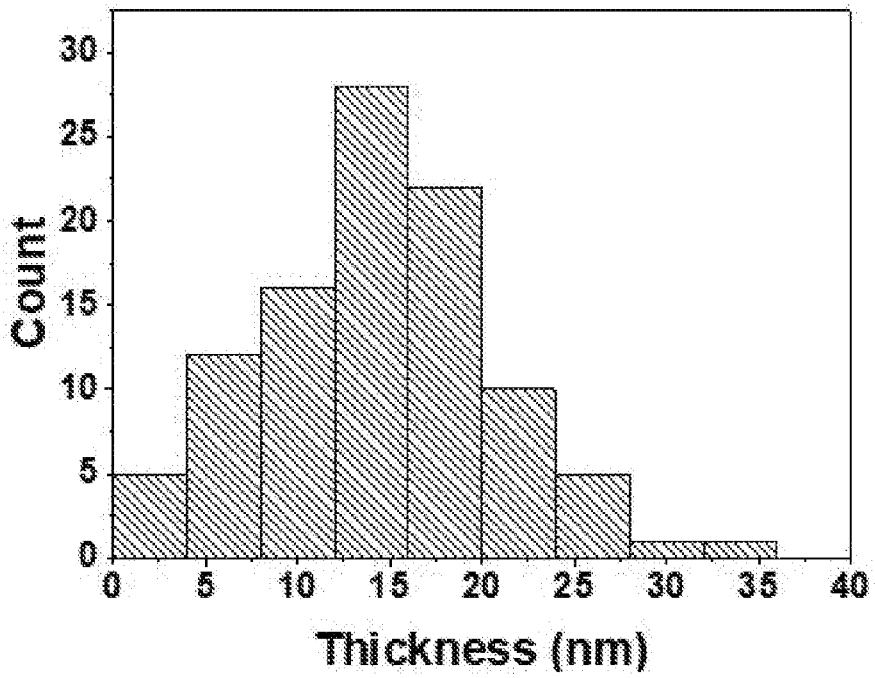

Fig. 5(c)

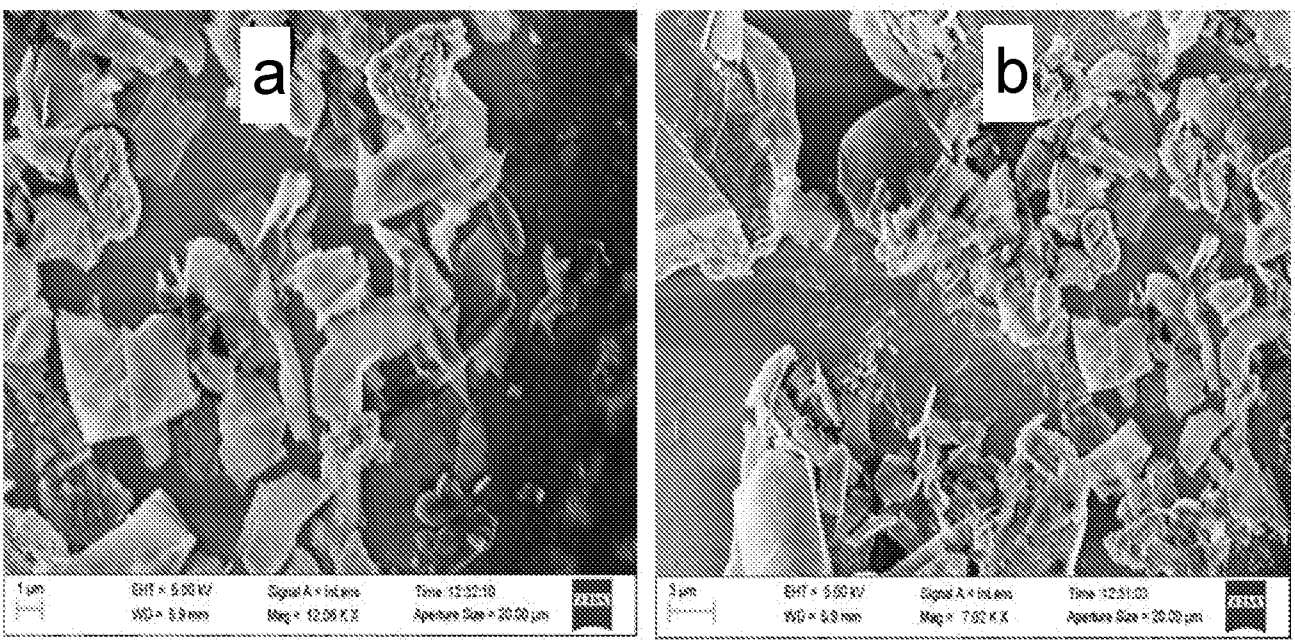

Fig. 6

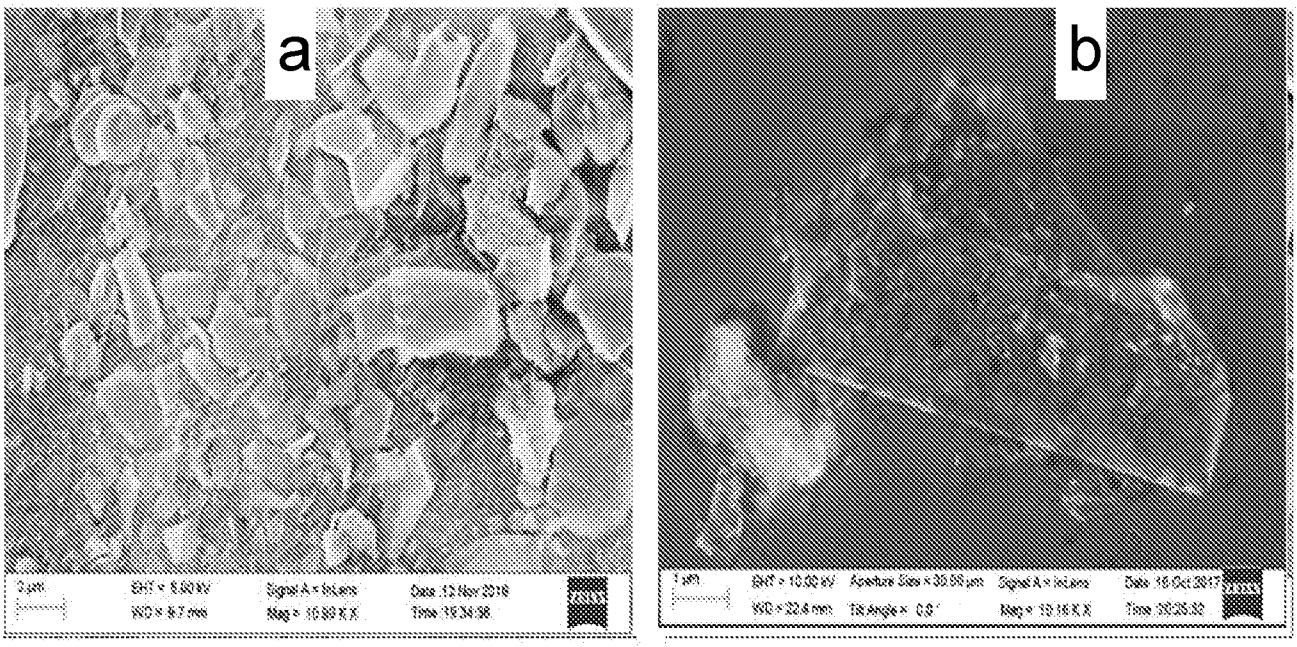

Fig. 7

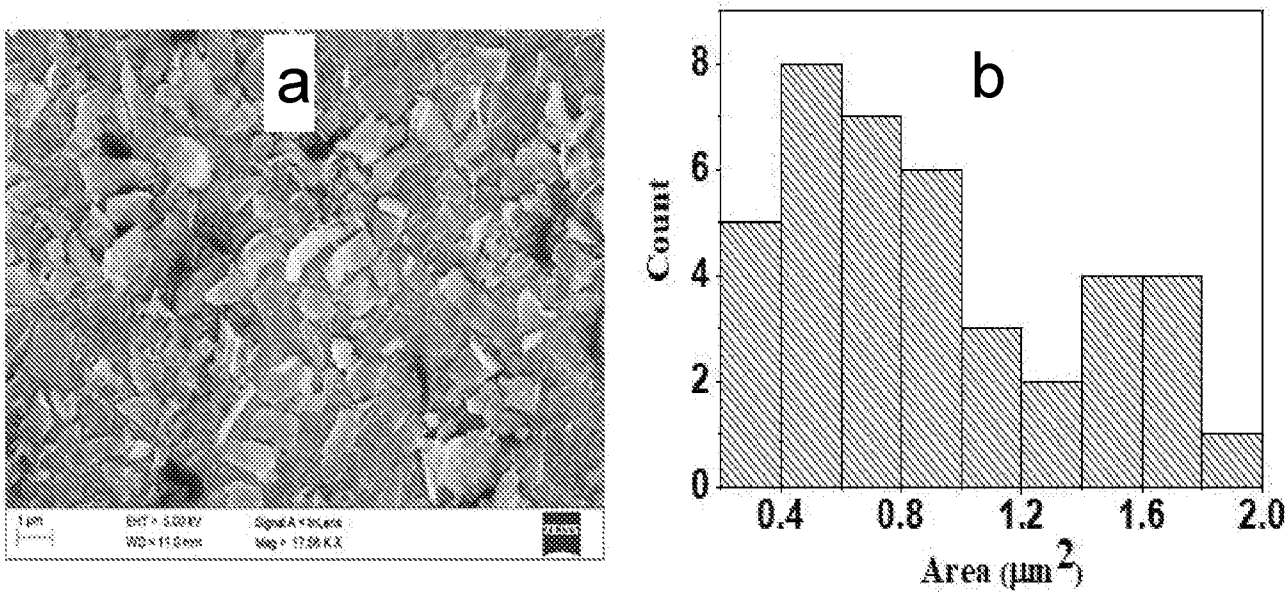

Fig. 8

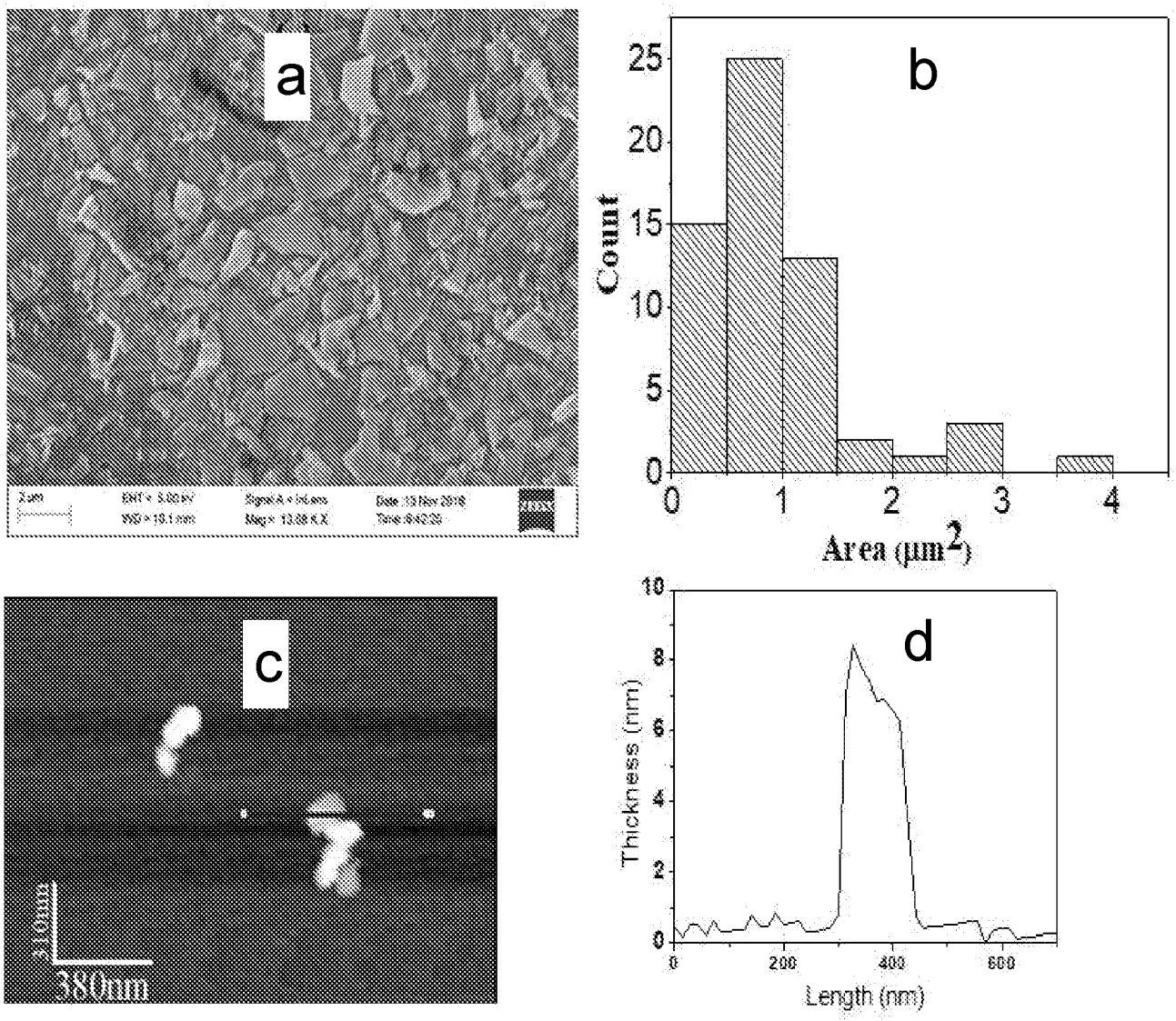

Fig. 9

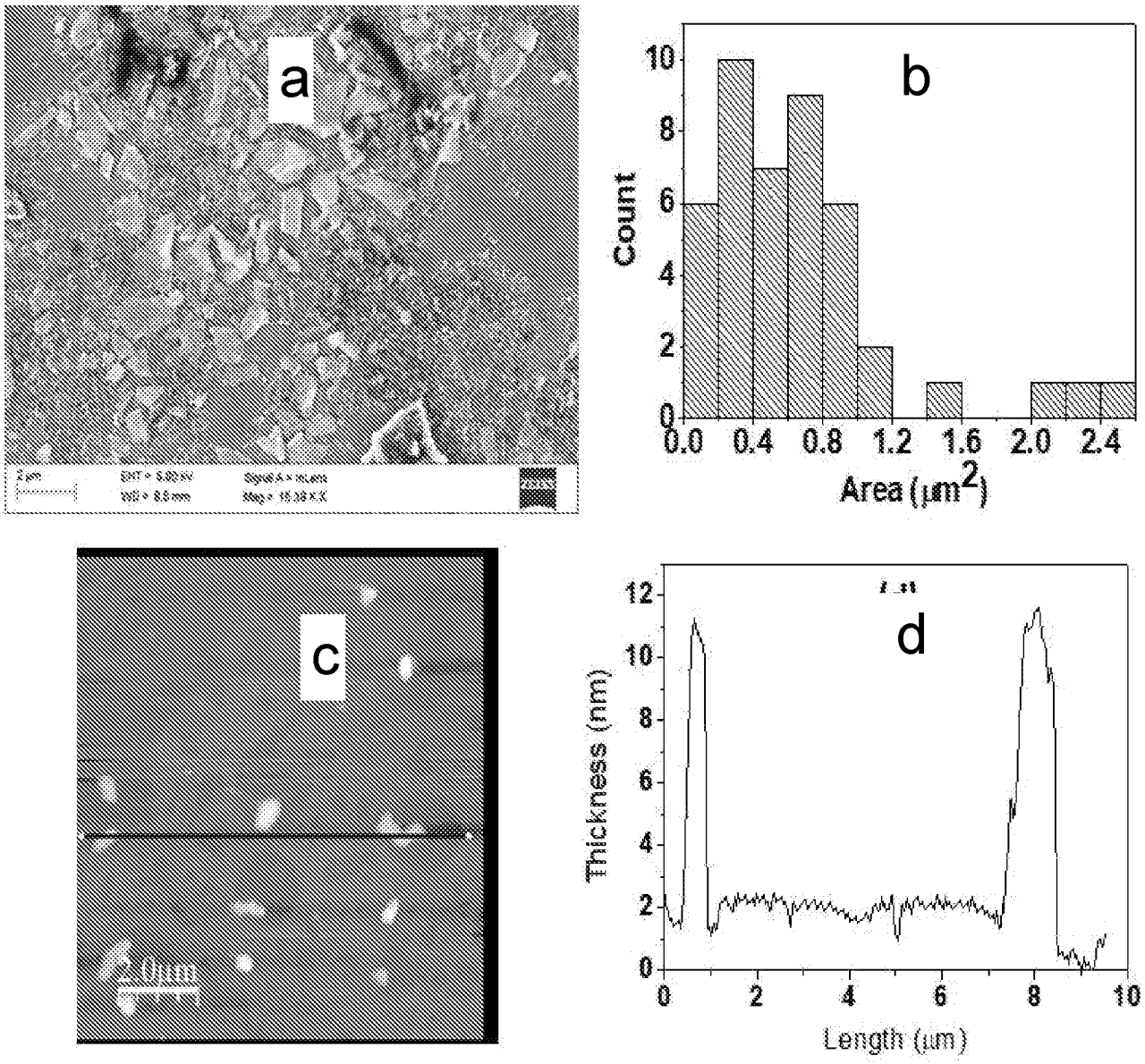

Fig. 10

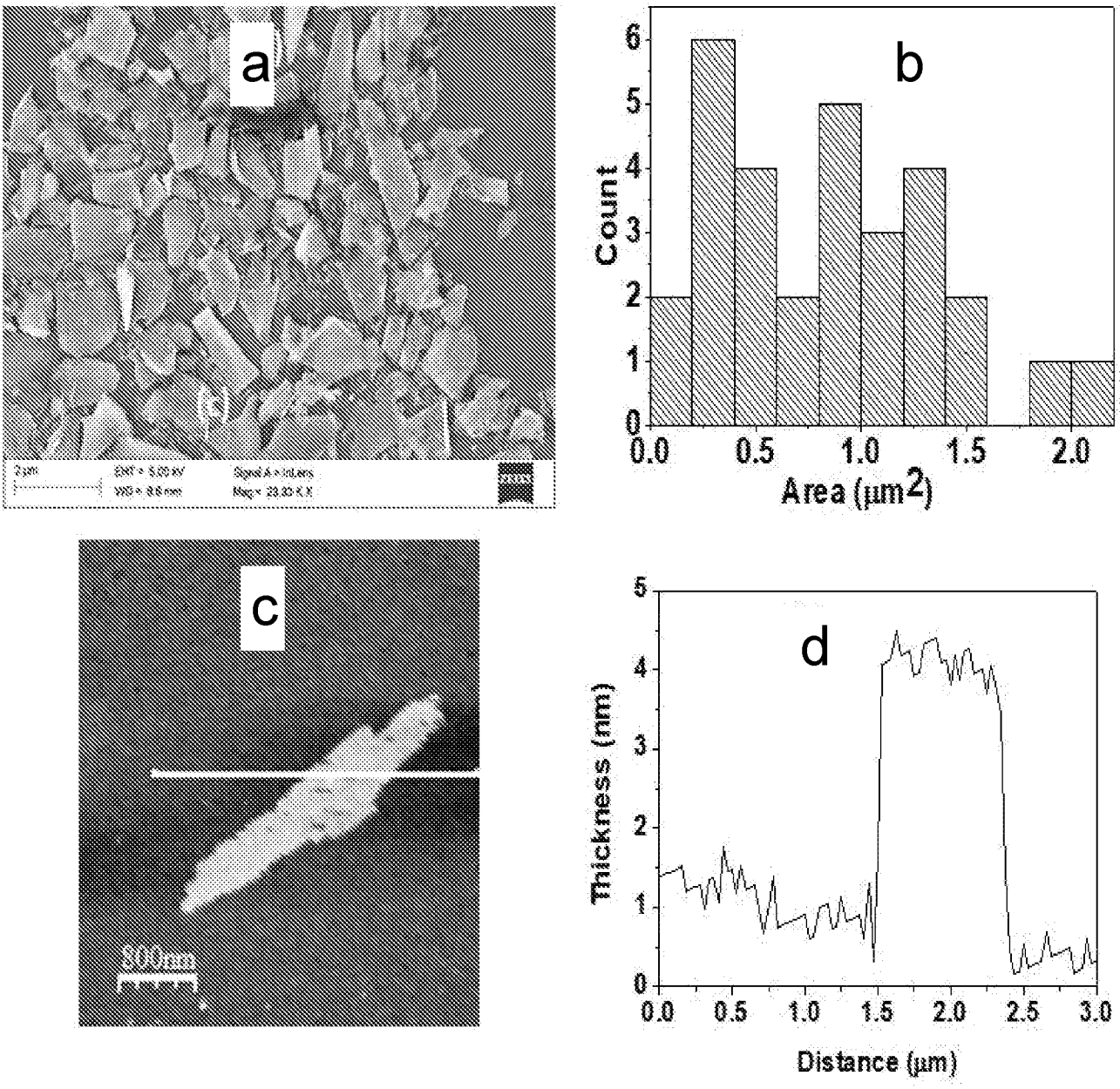

Fig. 11

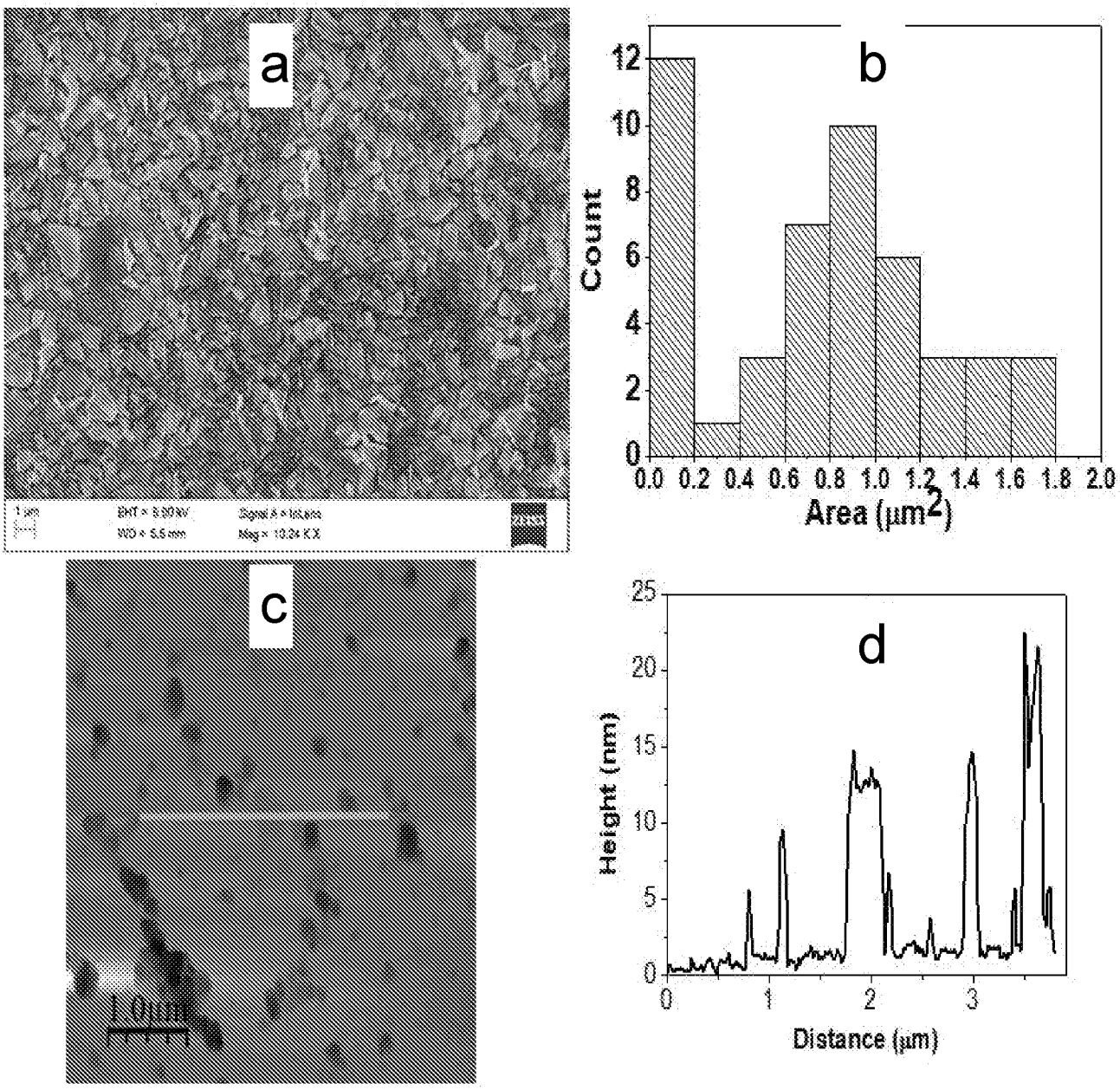

Fig. 12

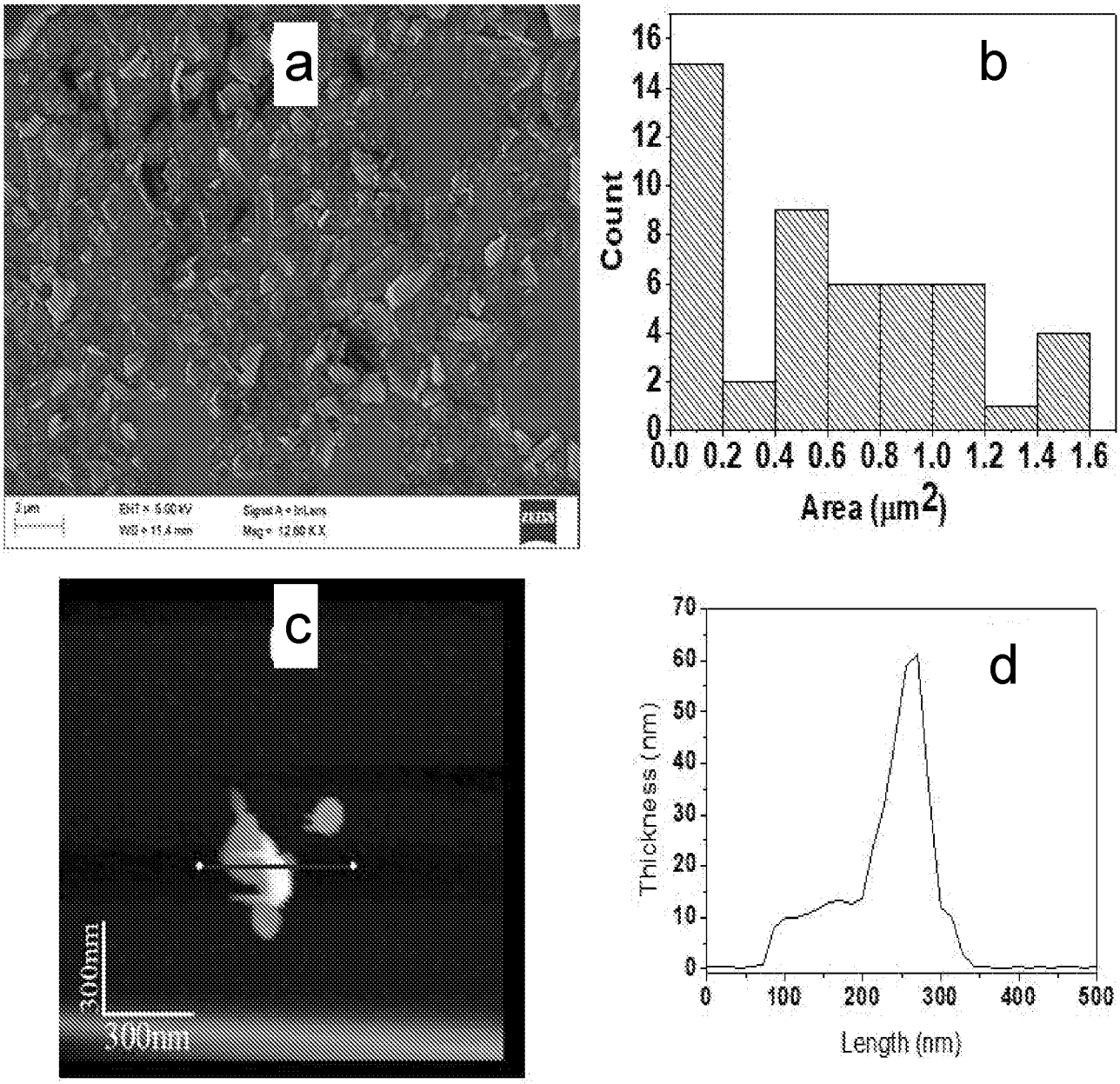

Fig. 13

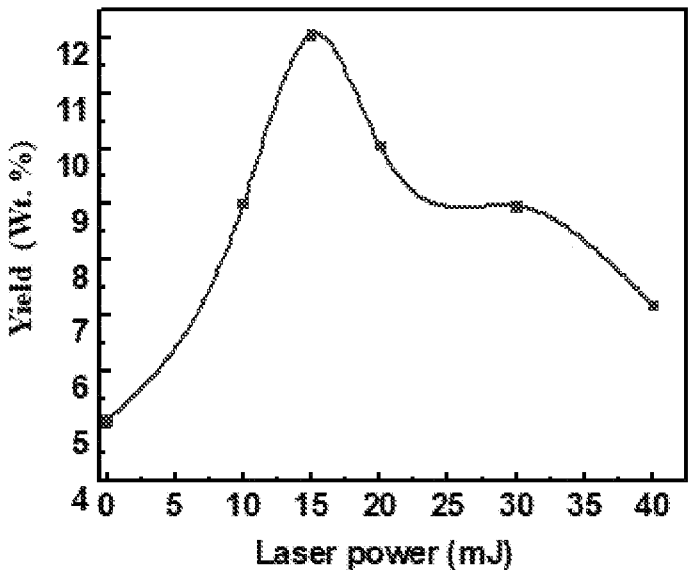

Fig. 14

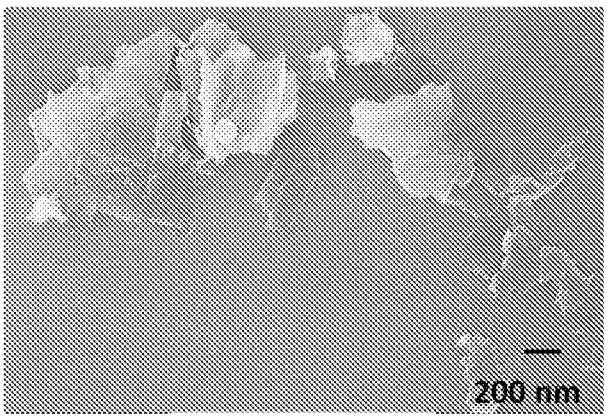

Fig. 15

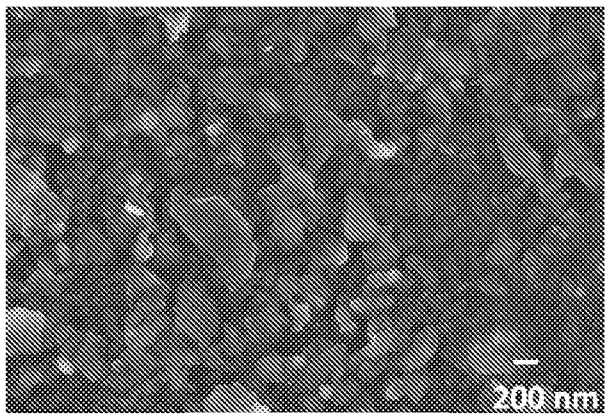

Fig. 16

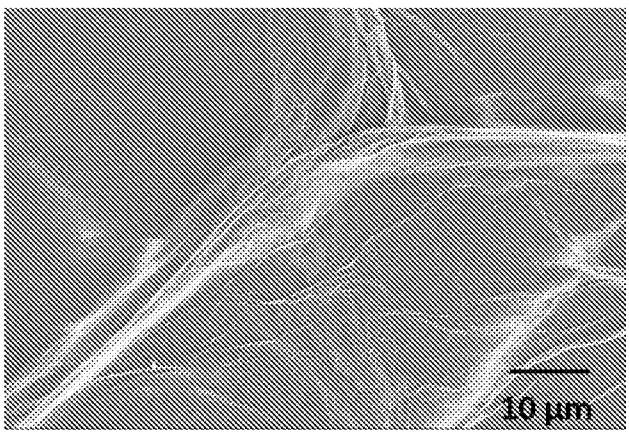

Fig. 17

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2020/050006

A. CLASSIFICATION OF SUBJECT MATTER
C01B32/00,B82Y30/00,B82Y40/00 Version=2020.01

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)

C01B, B82Y

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

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

Databases: Total Patent One, IPO Internal Database
Keywords: exfoliation, h-BN, laser, sonication, nanosheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Hu, S. L., Niu, K. Y., Sun, J., Yang, J., Zhao, N. Q., & Du, X. W. (2009). One-step synthesis of fluorescent carbon nanoparticles by laser irradiation. Journal of Materials Chemistry, 19(4), 484-488. 13 January 2009 (13-01-2009) URL: https://pubs.rsc.org/--/content/articlelanding/2009/jm/b812943f/unauth#!divAbstract [retrieved on 04-06-2020] Abstract, Introduction,	1-24
Y	Experimental Section; Figure 4. ---------- Kim, J., Kwon, S., Cho, D. H., Kang, B., Kwon, H., Kim, Y., ... & Lee, H. (2015). Direct exfoliation and dispersion of two-dimensional materials in pure water via temperature control. Nature communications, 6(1). 15 September 2015 (15-09-2015) URL: https://www.nature.com/articles/ncomms9294 [retrieved on 04-06-2020] Abstract, Results, Method Section 1, 2, 2.1, 4 & 5; Figures 1a-1c.	1-24

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

* Special categories of cited documents:
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"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08-06-2020	08-06-2020
Name and mailing address of the ISA/ Indian Patent Office Plot No.32, Sector 14,Dwarka,New Delhi-110075 Facsimile No.	Authorized officer Sunil Sharan Yadav Telephone No. +91-1125300200