



(11)

EP 4 563 227 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
04.06.2025 Bulletin 2025/23

(51) International Patent Classification (IPC):
B02C 17/20 (2006.01)

(21) Application number: **23212608.6**

(52) Cooperative Patent Classification (CPC):
B02C 17/20

(22) Date of filing: **28.11.2023**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL
NO PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(72) Inventors:
• **HAAG, Rainer**
12209 Berlin (DE)
• **BAWADKJI, Obida**
10407 Berlin (DE)

(74) Representative: **Maikowski & Ninnemann**
Patentanwälte Partnerschaft mbB
Postfach 15 09 20
10671 Berlin (DE)

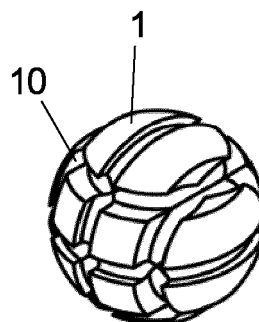
(71) Applicant: **Freie Universität Berlin**
14195 Berlin (DE)

(54) **BEAD FOR USE IN A MILLING DEVICE**

(57) The invention relates to a bead (1) for use in a milling device (20), the bead (1) having a general shape of a sphere and comprising a modified spherical surface structure (10), furthermore the invention relates to meth-

od for co-crystallization, to the method for allotrope conversion and to the method for particle size reduction, wherein said methods use said bead (1).

FIG 1



EP 4 563 227 A1

Description

[0001] The invention relates to a bead for use in a milling device. Beads of this kind can be used in a variety of mechanochemical processes.

[0002] Mechanochemistry is vastly applied in scientific research and industry. Mechanochemical processes are often conducted in a rotating chamber (of a milling device), the chamber being equipped with a milling medium. To control the mechanochemical processes as precisely as possible, it is important to understand the impact of the different process parameters. Process parameters are in particular running time, atmosphere (composition of gas, pressure) inside the milling device, milling energy (mainly determined by the rotational speed of the milling device and by the milling medium-to-educt weight ratio), material of the chamber and of the milling medium, and mass transfer. The mass transfer in a mechanochemical process is mainly dependent on the chamber volume, the filling ratio of educt and milling medium, the size and weight of the milling medium, the rotational speed of the chamber.

[0003] The object underlying the present invention is to enhance the mass transfer in a mechanochemical process which is conducted using a milling medium, in particular a bead or a plurality of beads.

[0004] Said object is achieved according to the invention by a bead with the features of claim 1. Specific embodiments of the invention are specified in the dependent claims.

[0005] Accordingly, the bead is adapted for use in a milling device and has a general shape of a sphere. The bead is characterized in that it comprises a modified spherical surface structure. Compared to a sphere, the sphere with the modified spherical surface structure has a greater surface while the general shape of a sphere is maintained.

[0006] The surface structure may comprise a recess (groove) and/or a protrusion. In particular, the surface structure may be realized by a recess and/or a protrusion or by a pattern thereof. The recess may be realized as a groove. The protrusion may be realized as a bulge. The surface structure (recess and/or protrusion) may have a thickness (extension along a radial direction of the sphere) that is about 1 % to 20% of the diameter of the sphere, preferably about 5% to 15% of the diameter of the sphere, more preferably about 10% of the diameter of the sphere.

[0007] It can be provided that the surface structure has an elongated form, extending along an extension direction. The cross-section of the surface structure (perpendicular to its extension direction) may be arc-shaped, in particular circular arc-shaped. Alternatively, the cross-section of the surface structure may be V-shaped.

[0008] In one embodiment, the surface structure comprises at least one ring (groove and/or protrusion). That is to say, the surface structure forms a pattern with at least one ring. The at least one ring may have a diameter which

is at least half the diameter of the sphere. For example, the at least one ring has a diameter which is as large as the diameter of the sphere.

[0009] In one embodiment, the surface structure has more than one ring, at least two rings. At least one first ring may extend in a first plane and at least one second ring may extend in a second plane. The first plane may be not parallel to the second plane. For example, the first plane may be perpendicular to the second plane. It can be provided that the surface structure has a plurality of separate rings that extend in separate planes that are parallel to one another. It is also conceivable that the surface structure has a plurality of first rings extending in first parallel planes and a plurality of second rings extending in second parallel planes. Here, the first planes may be not parallel (for example perpendicular) to the second planes.

[0010] For example, the distance between two parallel rings may be between 1/5 of the diameter of the sphere and 2/5 of the diameter of the sphere, preferably about 1/3 of the diameter of the sphere. In case of more than two rings that extend in parallel planes, it may be provided that the distance between two neighboring planes is the same for each pair of neighboring planes.

[0011] In one embodiment, the surface structure has three first rings extending in first parallel planes and three second rings extending in second parallel planes. Here, the first planes are perpendicular to the second planes.

[0012] The bead may comprise or be made of tungsten carbide, ceramic, stainless-steel, steel, carbon steel, rubber or polyurethane, high-quality plastics, zirconia, alumina, glass, or any material associated with those typically used for ball-mill devices.

[0013] The invention additionally relates to a milling device. The milling device generally comprises a chamber, a drive system for rotating the chamber and at least one bead according to the invention. The at least one bead is provided to be put into the chamber.

[0014] The milling device may be a planetary ball-mill. The planetary ball mill comprises at least one grinding jar (chamber) which is arranged eccentrically on a sun wheel (which is part of the drive system). The direction of rotation of the sun wheel is opposite to that of the grinding jar(s). Grinding balls (beads) are provided in the grinding jar(s). Coriolis forces act on the grinding balls and lead to a difference in speed between the grinding balls and grinding jars. The speed difference produces frictional and impact forces, leading to high dynamic energies.

[0015] The invention additionally relates to a method using mechanochemical processes. The mechanochemical process may comprise high energy planetary ball milling (HEPBM). In particular, the method may be a method for mechanosynthesis of chemical compounds, for chemical functionalization, for co-crystallization, a method for allotrope conversion or a method for particle size reduction. The methods are carried out using at least one bead according to the invention or a milling device according to the invention.

[0016] The method for co-crystallization of two or more compounds may comprise the steps of adding the two or more compounds and at least one bead to a chamber of a milling device and rotating the chamber over a specific period of time.

[0017] The method for allotrope conversion of a chemical element may comprise the steps of adding the chemical element and at least one bead to a chamber of a milling device and rotating the chamber over a specific period of time.

[0018] The method for particle size reduction of at least one compound may comprise the steps of adding the at least one compound and at least one bead to a chamber of a milling device and rotating the chamber over a specific period of time.

[0019] The invention is explained in more detail below by way of exemplary embodiments in connection with the drawings, in which:

- fig. 1 shows a perspective view of a bead according to an embodiment of the invention;
- fig. 2 shows a front view of the bead of figure 1;
- fig. 3 shows a side view of the bead of figure 1;
- fig. 4 schematically shows a milling device according to an embodiment of the invention;
- fig. 5 schematically shows the steps of a mechanochemical process;
- fig. 6 shows results of a co-crystallization process of nicotinamide and salicylic acid using beads as shown in figure 1;
- fig. 7 shows results of an allotrope conversion process of red phosphorus to black phosphorus using HEPBM and beads as shown in figure 1;
- fig. 8 shows results of a particle size reduction process of TiO_2 particles using HEPBM and beads as shown in figure 1;
- fig. 9 shows the temperature distribution in a chamber of a milling device comprising beads as shown in figure 1; and
- fig. 10 shows the distribution of contact points of the bead shown in figure 1 realized by an ink print of the rolling bead.

[0020] Figure 1 shows a perspective view of a bead 1 according to one embodiment. The bead 1 has a general shape of a sphere. Its spherical surface is provided with a modified surface structure 10. The surface structure 10 is realized by recesses formed in the surface. The surface structure 10 comprises three first rings 11 and three

second rings 12 (Figures 2 and 3). The first rings 11 are arranged in separate (first) planes that are parallel to one another. The second rings 12 are arranged in separate (second) planes that are parallel to one another.

- 5 The (first) planes of the first rings 11 and the (second) planes of the second rings 12 are perpendicular to one another. The central first ring and the central second ring each have a diameter that is the same as the diameter of the sphere. The bead 1 (sphere) has a diameter of 10 mm. Other diameters, such as 5 mm, 15 mm, 20 mm, are possible. The recesses forming the modified surface structure 10 have a depth of 1mm. Generally, the depth (or thickness) of the surface structure may be about 10% of the diameter of the bead 1 (sphere). Each pair of neighboring parallel rings has the same distance, namely within a range of 20 - 40% of the bead's diameter. For example, the distance between two neighboring parallel rings is 3.11 mm, with a bead diameter of 10mm and with three parallel rings.

- 20 **[0021]** Figure 4 schematically shows a milling device 20 according to one embodiment. The milling device comprises a chamber 21 and a drive system 22. The chamber 21 is adapted to receive a plurality of beads 1 and one or more compounds / agents provided to undergo a mechanochemical process. The chamber 21 is rotatably mounted and adapted to rotate about a rotation axis. The drive system 22 is adapted to rotate the chamber 21 about its rotation axis.

- 25 **[0022]** Figure 5 schematically shows the general steps of a mechanochemical process. The mechanochemical process includes a first step 100 of adding one or more compounds / chemical elements and at least one bead 1 to a chamber 21 of a milling device 20 and a second step 200 of rotating the chamber 21 over a specific period of time.

- 30 **[0023]** For testing purposes, the bead 1 shown in Figures 1 to 3 (made of stainless-steel) has been used in the methods that will be described in the following with reference to the figures 6 to 8. In the following the bead 1 shown in Figures 1 to 3 is also referred to as MBMM bead.

- 35 **[0024]** First, a plurality of beads 1 have been used in a method for co-crystallization of nicotinamide (first compound) and salicylic acid (second compound) to form the hydrogen bonded co-crystal NicSal. The reaction equation is indicated in subfigure a) of Figure 6. Nicotinamide and salicylic acid were combined in a 1:1 molar ratio (for example 488 mg of nicotinamide ($\geq 99,5\%$ Sigma Aldrich) and 552 g of salicylic acid ($\geq 99,0\%$ Sigma Aldrich)). In this method, six beads 1 have been used to reach a ball to powder ratio of 25:1. Nicotinamide, salicylic acid and beads 1 of the type shown in Figures 1 to 3 were filled in a stainless-steel chamber 21 of 80 ml, the chamber 21 was sealed and placed in a milling device 20 (HEPBM device). The chamber 21 was rotated at 600 rpm for approximately 1 hour. The reaction has been monitored via Raman spectroscopy. For this purpose, a sample was extracted from the chamber 21 every 10 minutes. For reference, in subfigure b) of Figure 6 the Raman spectra

of nicotinamide, salicylic acid and NicSal are indicated in a range from 30 to 2000 cm^{-1} . In particular, the range between 30 and 200 cm^{-1} and the peak at about 770 cm^{-1} have been monitored to measure the turnover of the mechanochemical process. The spectra with the label MBMM refer to the process using beads 1 as shown in Figures 1 to 3 (modified ball-mill medium). The spectra with the label NBMM are reference spectra and refer to the same process using beads having a general shape of a sphere without surface structure (normal ball-mill medium). From these spectra it can be seen that the Raman bands between 30 and 200 cm^{-1} representative of NicSal appear immediately (10 minutes) and that the peak at about 770 cm^{-1} representative of salicylic acid disappears immediately (10 minutes) using the MBMM beads 1 of Figures 1 to 3, while the NBMM beads without surface structure produce such a turnover only after one hour approximately. A semiquantitative analysis has been performed to determine the turnover by plotting the intensity ratios of the evolving Raman band I_{795} at 795 cm^{-1} corresponding to NicSal against the depleting Raman band I_{778} at 778 cm^{-1} corresponding to salicylic acid according to following equation

$$\text{Turnover (a. u.)} = \frac{I_{795}}{(I_{778} + I_{795})}$$

[0025] The turnover is shown in subfigure c) of Figure 6. The values reached with the MBMM beads 1 (squares) rise immediately and stay at the level reached over time. The values reached with the NBMM beads (circles) rise more slowly and more or less linearly.

[0026] Second, a plurality of beads 1 have been used in a method for allotrope conversion of red phosphorus to form black phosphorus. The reaction equation is indicated in subfigure a) of Figure 7. Red phosphorus (1g, $\geq 97,0\%$ Merck) was sealed together with a mixture of MBMM beads 1 (with surface structure) and NBMM beads (without surface structure) with a ratio 1:4 of MBMM beads to NBMM beads in a (stainless-steel) chamber 21 (planetary ball-mill chamber) of 80 ml under argon (9-10 mbar, to prevent degradation of black phosphorus). The chamber 21 was rotated at 600 rpm for approximately 4 hours. The ratio of the mixture of beads to red phosphorus was a 50:1 BPR (ball to powder ratio), using 12 beads in total. The allotrope conversion process was monitored by extracting a sample every hour. The samples were subject to Raman spectroscopy in the range of 300 to 500 cm^{-1} where the spectral profiles of black phosphorus and red phosphorus are distinctive. In particular, the B_1 peak at approximately 350 cm^{-1} of red phosphorus, the A_g^1 peak at approximately 360 cm^{-1} of

black phosphorus, the B_{2g} peak and the A_g^2 peak of black phosphorus at 435 cm^{-1} and 463 cm^{-1} , respectively, have been monitored. Additionally, visual observation of

the color change of the reaction product from red to black can give a simple indication on the mechanochemical transformation turnover (not shown).

[0027] The spectra with the label MBMM (subfigure b) of Figure 7) refer to the process using the mixture of beads described above. The spectra with the label NBMM (subfigure c) of Figure 7) are reference spectra and refer to the same process using only NBMM beads having a general shape of a sphere without surface structure (normal ball-mill medium).

[0028] The Raman spectra, in particular the pronounced B_{2g} peak and the A_g^2 peak of black phosphorus at 435 cm^{-1} and 463 cm^{-1} , respectively, indicate an effective allotrope conversion using the mixture of beads including the beads 1 of Figures 1 to 3. Also the broad band between 368 and 425 cm^{-1} is efficiently

depleted, while the A_g^1 peak at approximately 360 cm^{-1} is clearly pronounced. In comparison, the NBMM beads without surface structure are not able to convert the red phosphorus with this efficiency. With NBMM beads only, said Raman bands do not significantly evolve even after 4 hours.

[0029] Third, a plurality of beads 1 have been used in a method for particle size reduction of titanium dioxide (TiO_2) particles. Titanium dioxide (1g, 99,0% Riedel-de Haën) and six beads 1 as shown in Figures 1 to 3 with a ball to powder ratio of 25:1 have been filled in a stainless-steel chamber 21 of 80 ml. The chamber 21 was sealed and placed in a milling device 20 (HEPBM device). The chamber was rotated at 600 rpm for approximately 15 minutes. The process has been monitored via dynamic light scattering (DLS). For this purpose, a sample has been extracted from the chamber 21 every 5 minutes.

[0030] The spectra in Figure 8 with the label MBMM refer to the process using the beads 1 of Figures 1 to 3. The spectra in Figure 8 with the label NBMM are reference spectra and refer to the same process using only beads having a general shape of a sphere without surface structure (normal ball-mill medium). As can be seen from the spectra (see subfigure a) of Figure 8), the MBMM beads 1 are able to reduce the average particle size of TiO_2 to approximately 660 nm in hydrodynamic diameter within 5 minutes, whereas the NBMM beads need 15 minutes to achieve this particle size. Additionally, the monodispersity of the milled particles is improved when using MBMM beads. Subfigure b) of Figure 8 shows a plot of the average particle size over time using the (MBMM) beads of Figures 1 to 3 (continuous line) or (NBMM) beads without a surface structure (dashed line).

[0031] The successful co-crystallization of nicotinamide and salicylic acid, the successful allotrope conversion of red phosphorus to black phosphorus and the successful particle size reduction of titanium dioxide can be attributed to the modified spherical surface structure 10 which is adapted for mixing particulate matter. The surface structure 10 allows for effective penetration

into particulate matter and mixing the particles throughout its depth, resulting in uniform mixing. This mixing leads to the breaking up of formed clumps, preventing caking and resulting in a homogeneous mass transfer of reactants inside the chamber. The beads 1 with the surface structure 10 thus serve as homogenizing agent.

[0032] On the other hand, beads without this surface structure have a smooth surface which prevents deep penetration and slides on the particle surface, leading to caking and uneven mixing. This causes non-uniform mass transfer of particles in the chamber.

[0033] A factor contributing to the high turnover in the methods described above using beads according to Figures 1 to 3 is the kinetic energy that is generated by the beads 1 in the rotating chamber 21. The kinetic energy generated is higher than that generated by beads without this surface structure as the contact frequency with the inner surface of the chamber 21 is increased due to the surface structure 10. The distribution of contact points is shown in Figure 10 where subfigure a) shows the distribution of contact points of a NBMM bead without surface structure and subfigure b) shows the distribution of contact points of a MBMM bead 1 with surface structure 10. To visualize the distribution of contact points a bead has been covered with ink and controllably rolled on a straight line on a sheet of paper. A greater number of contact points leads to more shearing and friction inside the chamber 21 during the milling procedure, which results in a greater distribution of contact points and greater amount of kinetic energy output.

[0034] Without the presence of additional materials (chemical elements / compounds provided to undergo a mechanochemical process) inside the chamber, the kinetic energy is dissipated into the chamber in the form of heat. Figure 9 shows the temperature of the chamber 21 in 10 minute intervals of milling at 600 rpm using 6 beads weighing 25 g altogether. The first row (labeled with NBMM) shows thermal images of the chamber filled with spherical beads without surface structure, while the second row (labeled with MBMM) shows thermal images of the chamber filled with spherical beads 1 with surface structure 10 as shown in Figures 1 to 3. The thermal images were captured using a forward looking infrared (FLIR) camera. It can be clearly seen from the thermal images, that the greater kinetic energy produced by the beads of Figures 1 to 3 leads to a higher average temperature of the chamber 21 as compared to the beads without surface structure (NBMM). In addition, the spatial distribution of the kinetic energy generated by the beads of Figures 1 to 3 is greater. The higher number of contact points distributes the kinetic energy over a larger area / in a larger space within the chamber, creating a homogeneous environment for chemical conversions resulting in higher quality products produced more efficiently.

[0035] The methods described above are performed without solvents or liquids. However, a small amount of liquid may be added as a dispersing agent. Such a method is referred to as liquid-assisted grinding.

Experimental details

General

- [0036]** All methods described above were performed using "Pulverisette 6" mono mill from FRITSCH GmbH.

Raman spectroscopy

- [0037]** Raman spectroscopy measurements were done using a Horiba Xplora spectrometer equipped with an x/y piezo stage. Laser excitation for all measurements was set at 532 nm which was delivered through a 100x objective (Nikon®). To avoid thermal heating and/or degradation of the samples, the laser power was filtered to 1 % of the intensity for all measurements. All spectra were measured with 1 second accumulation time. Samples were deposited on silicon dioxide/silicon wafers (1 cm x 1 cm).

- [0038]** Statistical Raman spectroscopy (SRS) was conducted by measurement of Raman maps over sample regions deposited on the Si or SiO₂/Si substrates. The average spectra were calculated from the maps and the Si-only spectra were filtered out. Accumulation time for each spectrum was set to 1 second. Substrate movement for the mapping was done using the motorized x/y piezo stage.

Dynamic light scattering

- [0039]** DLS data were measured using a Malvern Zetasizer Nano device (Brookhaven Instruments Corp.) at room temperature (25 °C). The TiO₂ sample concentrations were set at 1 mg mL⁻¹ concentration in 1% citric acid aqueous solutions (w/w). For every sample, three measurement runs were recorded, and the average of the results was used.

Thermal assessment using FLIR

- [0040]** NBMM or MBMM (6 units, 25:1 BPR) was placed in the 80 mL stainless-steel ball-mill chamber and sealed before transferring it to the ball-mill. The ball-mill operated at 200-600 rpm for a duration of 10 to 60 min depending on the intent of the experiment. A FLIR camera (FLIR, 0-350 °C, Model EX, FLIR® Systems) fixed onto a tripod was placed in a set position pointing towards a designated place for the ball-mill chamber for consistent capturing of the thermal images.

Claims

1. A bead (1) for use in a milling device (20), the bead (1) having a general shape of a sphere and comprising a modified spherical surface structure (10).
2. The bead (1) as claimed in claim 1, **characterized in**

that the surface structure (10) comprises a recess and/or a protrusion.

3. The bead (1) as claimed in claim 1 or 2, **characterized in that** surface structure (10) comprises at least one ring (11, 12). 5
4. The bead (1) as claimed in claim 3, **characterized in that** the at least one ring (11, 12) has a diameter which is at least half the diameter of the sphere. 10
5. The bead (1) as claimed in claim 3, **characterized in that** the at least one ring (11, 12) has a diameter which is as large as the diameter of the sphere. 15
6. The bead (1) as claimed in one of claims 3 to 5, **characterized in that** the surface structure (10) has at least one first ring (11) extending in a first plane and at least one second ring (12) extending in a second plane, wherein the first plane is perpendicular to the second plane. 20
7. The bead (1) as claimed in one of claims 3 to 5, **characterized in that** the surface structure (10) has a plurality of separate rings (11, 12) that extend in separate planes that are parallel to one another. 25
8. The bead (1) as claimed in one of claims 3 to 7, **characterized in that** the surface structure (10) has a plurality of first rings (11) extending in first parallel planes and a plurality of second rings (12) extending in second parallel planes, wherein the first planes are perpendicular to the second planes. 30
9. The bead (1) as claimed in one of claims 3 to 8, **characterized in that** the surface structure (10) has three first rings (11) extending in first parallel planes and three second rings (12) extending in second parallel planes, wherein the first planes are perpendicular to the second planes. 35 40
10. Milling device (20) comprising a chamber (21), a drive system (22) for rotating the chamber (21) and at least one bead (1) according to one of the preceding claims, the at least one bead (1) being provided to be put into the chamber (21). 45
11. Method for co-crystallization of two or more compounds comprising 50
 - adding the two or more compounds and at least one bead (1) to a chamber (21) of a milling device (20), and
 - rotating the chamber (21) over a specific period of time 55

wherein the at least one bead (1) is a bead (1) according to one of claims 1 to 9 and/or the milling

device (20) is a milling device (20) according to claim 10.

12. Method for allotrope conversion of a chemical element comprising
 - adding the chemical element and at least one bead (1) to a chamber (21) of a milling device (20), and
 - rotating the chamber (21) over a specific period of time

wherein the at least one bead (1) is a bead (1) according to one of claims 1 to 9 and/or the milling device (20) is a milling device (20) according to claim 10.
13. Method for particle size reduction of at least one compound comprising
 - adding the at least one compound and at least one bead (1) to a chamber (21) of a milling device (20), and
 - rotating the chamber (21) over a specific period of time

wherein the at least one bead (1) is a bead (1) according to one of claims 1 to 9 and/or the milling device (20) is a milling device (20) according to claim 10.

FIG 1

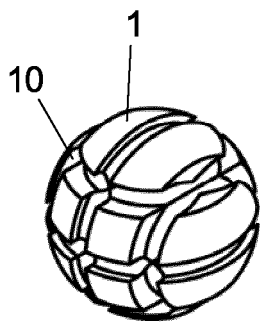


FIG 2

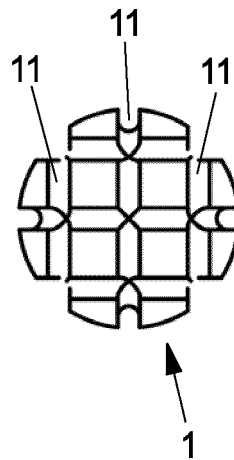


FIG 3

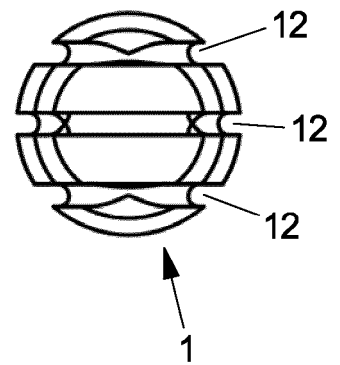


FIG 4

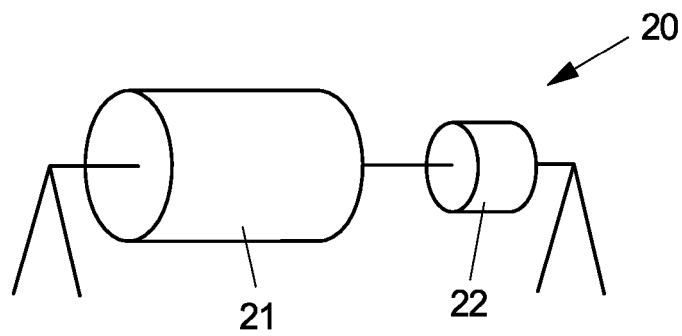


FIG 5

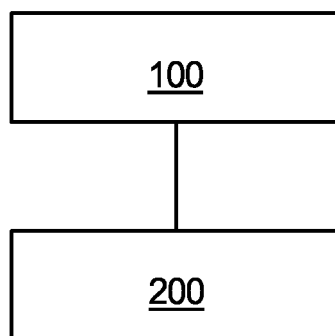


FIG 6

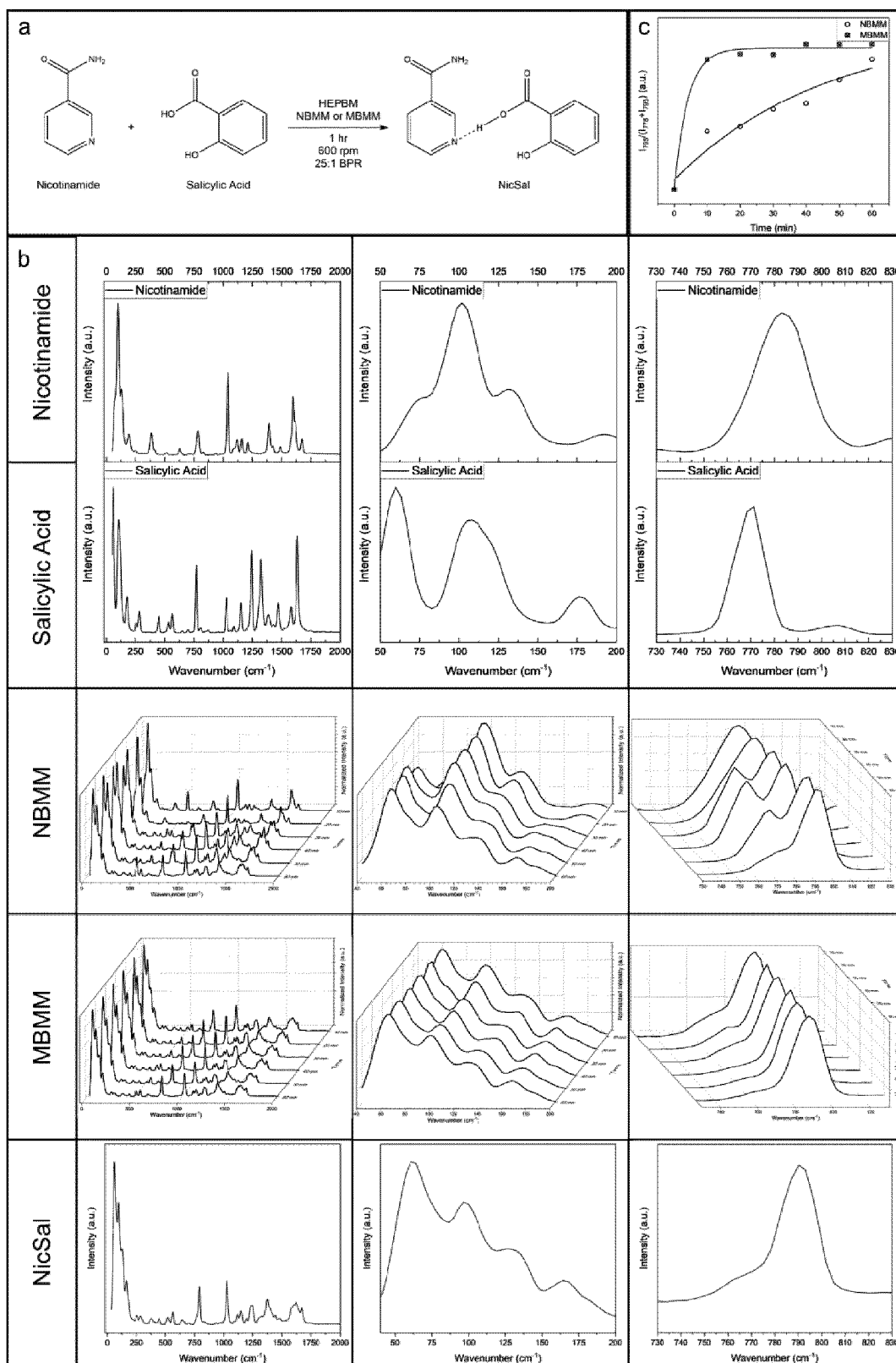


FIG 7

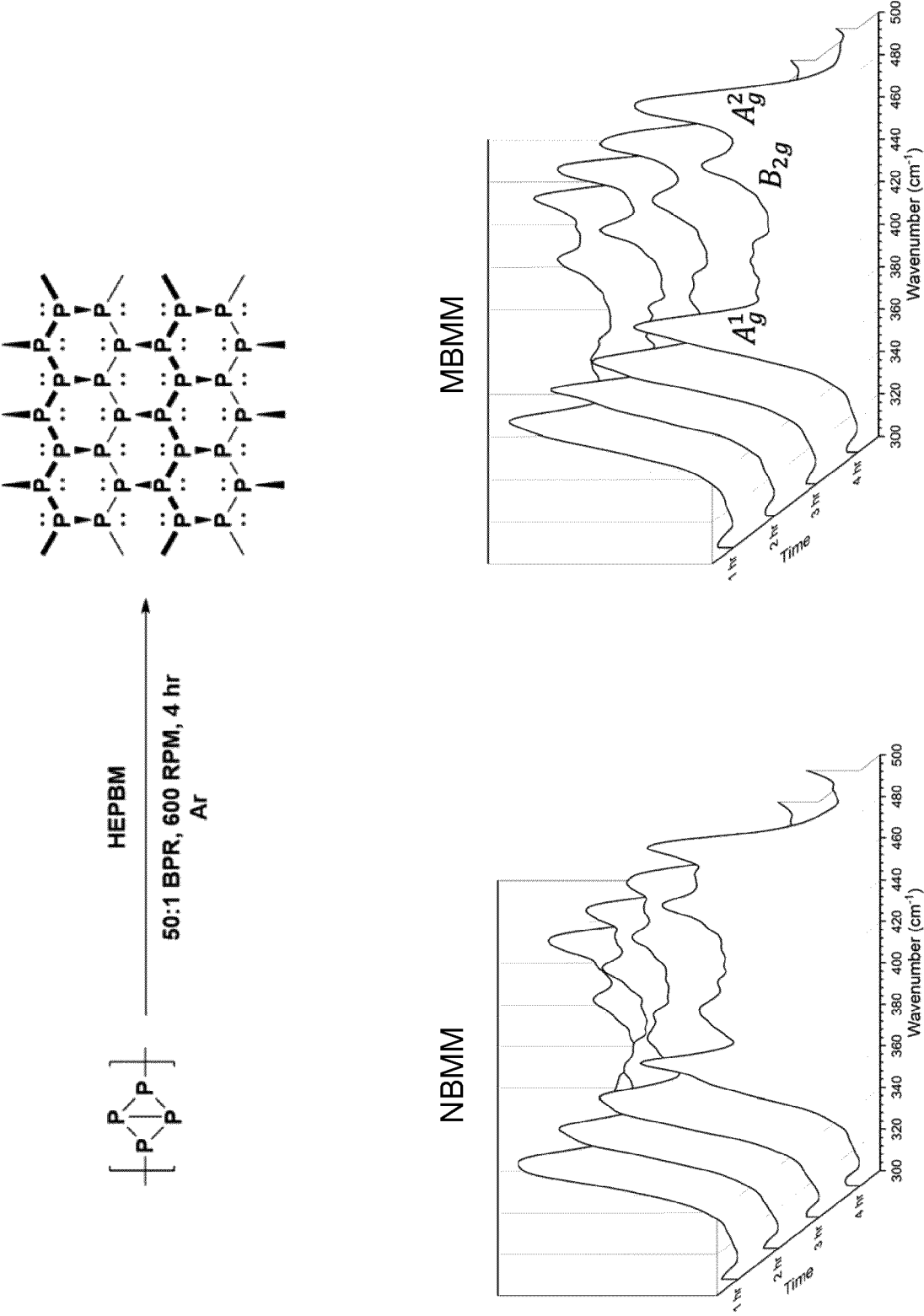


FIG 8

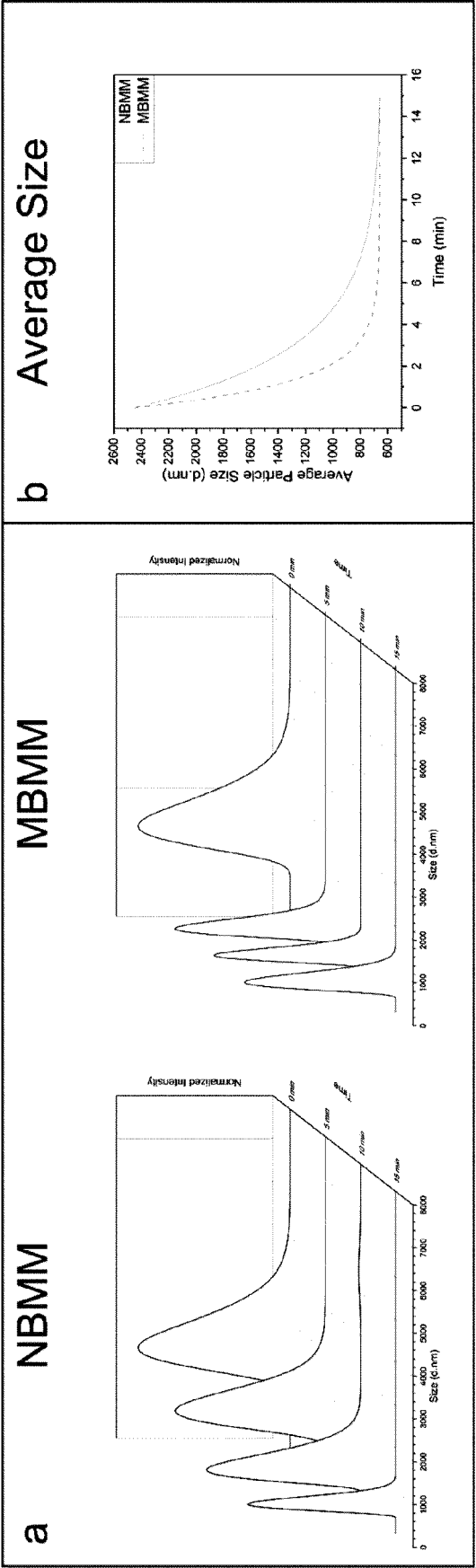


FIG 9

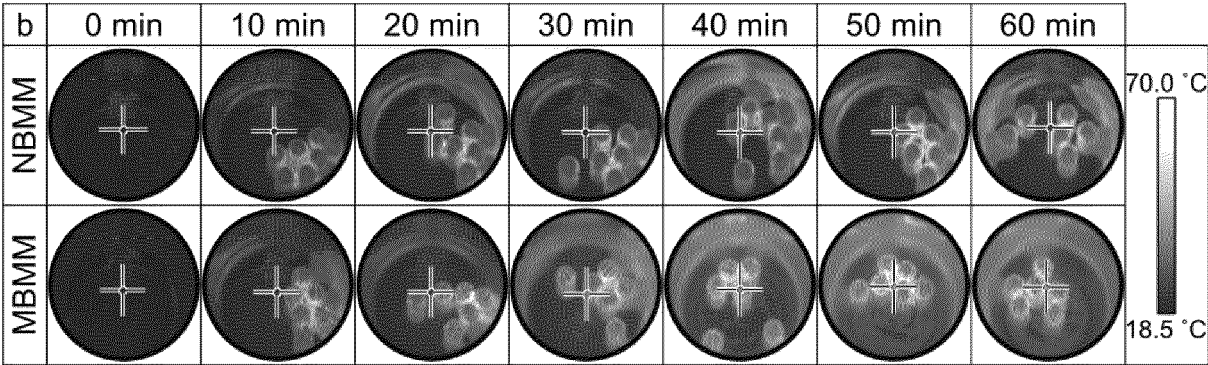


FIG 10





EUROPEAN SEARCH REPORT

Application Number

EP 23 21 2608

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 2 359 945 A1 (NAT INST FOR MATERIALS SCIENCE [JP]) 24 August 2011 (2011-08-24)	1-10, 13	INV. B02C17/20
Y	* paragraph [0038] * * paragraph [0040] * * paragraph [0042] * * paragraph [0046] - paragraph [0056] * * paragraph [0070] * * paragraph [0074]; figures 9, 10, 14-15, 17-19; table 4 *	11, 12	
Y	GRÖLS JAN ROLAND ET AL: "Mechanochemical co-crystallization: Insights and predictions", COMPUTERS & CHEMICAL ENGINEERING, PERGAMON PRESS, OXFORD, GB, vol. 153, 27 June 2021 (2021-06-27), XP086726578, ISSN: 0098-1354, DOI: 10.1016/J.COMPHEMENG.2021.107416 [retrieved on 2021-06-27]	11	
A	* abstract * * page 1, column 1 - column 2 * * page 2, column 1 - column 2 * * table 2 * * page 5, column 2 * * page 6, column 1 *	1, 10	TECHNICAL FIELDS SEARCHED (IPC) B02C B01J
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 5 April 2024	Examiner Jovanovic, Mihajlo
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	



EUROPEAN SEARCH REPORT

Application Number

EP 23 21 2608

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	LIU CHENG ET AL: "A Review on Applications of Layered Phosphorus in Energy Storage", TRANSACTIONS OF TIANJIN UNIVERSITY, EDITORIAL BOARD OF TRANSACTIONS OF TIANJIN UNIVERSITY, TIANJIN, CN, vol. 26, no. 2, 20 January 2020 (2020-01-20), pages 104-126, XP037072920, ISSN: 1006-4982, DOI: 10.1007/s12209-019-00230-X [retrieved on 2020-01-20]	12	
A	* abstract * * page 106, column 1 * -----	1,10	
			TECHNICAL FIELDS SEARCHED (IPC)
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
Munich		5 April 2024	Jovanovic, Mihajlo
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

1

EPO FORM 1503 03.82 (P04C01)

05-04-2024

EPO FORM P0459

14