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(54) Title: NANOTUBES, PROCESS FOR OBTAINING THEM AND CEMENTITIOUS COMPOSITIONS COMPRISING THEM

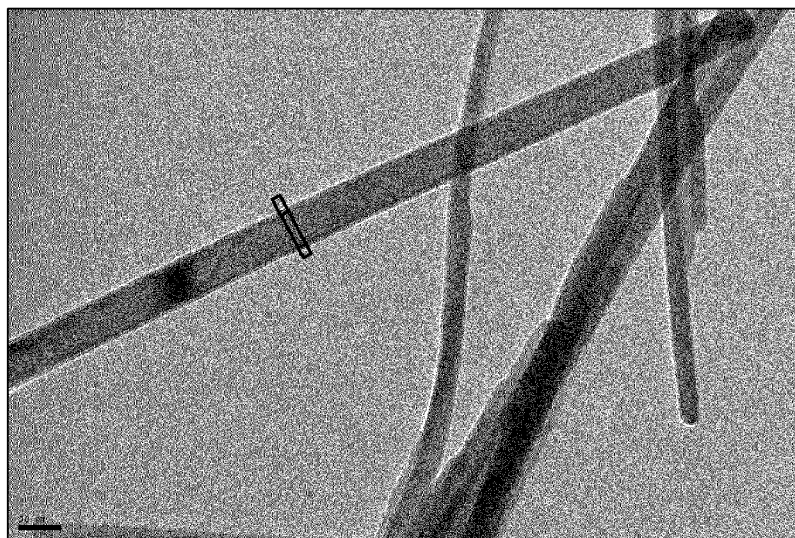


Fig. 6

(57) Abstract: The present invention describes the preparation of nanotubes made from portlandite, the naturally occurring form of calcium hydroxide, $\text{Ca}(\text{OH})_2$. Portlandite nanotubes are obtained by a process comprising the following steps: a) reacting calcium chloride with calcium oxide in aqueous solution, thus obtaining an aqueous dispersion; b) feeding as such the aqueous dispersion obtained in step a) to a hydrothermal reaction, thus obtaining portlandite nanotubes. The invention also concerns the use of the portlandite nanotubes as a component for cementitious compositions to provide reinforced mortar or concrete.



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Nanotubes, process for obtaining them and cementitious compositions comprising them.

FIELD OF THE INVENTION

The present invention describes the preparation of nanotubes made from
5 portlandite, the naturally occurring form of calcium hydroxide, $\text{Ca}(\text{OH})_2$.

BACKGROUND OF THE INVENTION

Cement-based materials are largely used in buildings especially for their resistance to compression. However these materials generally show a brittle response under tensile stress.

10 In order to overcome this deficiency, concrete is often strengthened by introducing reinforcing materials in the cementitious matrix, primarily such as steel rods or fibres, usually randomly oriented microfibres made from steel, glass or polymeric materials. The main aim of the use of steel rods is to prevent macro-cracking that could lead to structural failure, whilst the use of microfibers is mainly meant to
15 reduce the formation of micro-cracks, usually brought about by autogeneous and drying-related shrinkage at the start of the hydration stage, and to inhibit the development of those micro-cracks into macro-cracks. However, since rods and microfibres mainly exert their structural function at higher scales, the above approaches to reinforcement do not take into sufficient account chemical and
20 mechanical damages that could originate at the nanoscale inside concrete. In fact, a way to improve the properties of cement-based materials would be to fine-tune their nanostructure, a goal attempted in many ways but yet to be accomplished.

Several approaches have been proposed to improve the characteristics of the cementitious nanostructure. One of the approaches is the development of nano-
25 fibres to refrain nano-cracks from forming and developing. See M. S. Konsta-Gdoutos, Z. S. Metaxa, S. P. Shah, Cem. Concret Compos. 2010, 32, 110.

Nanotubes are nanometer-scale tube-like structures. Due to their high mechanical properties, tensile strength, elastic modulus and aspect ratio, nanotubes made from

carbon (CNTs) have been suggested to be an ideal reinforcement material, see for example M. Endo, S. Iijima, M. S. Dresselhaus, Carbon nanotubes, Pergamon Press, Oxford, UK, 1997; M. R. Falvo, G. J. Clary, R. M. Taylor, V. Chi, F. P. Brooks, S. Washburn, R. Superfine Nature 1997, 389, 582; S. Iijima, T. Ichihashi Nature
5 1993, 364, 737.

However, since carbon nanotubes are hydrophobic, it must be taken into account that their chemical nature is quite different from the inorganic minerals that form a cementitious matrix, so that CNTs would tend to bundle up, which makes it difficult to disperse them homogeneously and have them finally anchored to a cementitious
10 matrix. Due to these reasons, CNTs turn out to be difficult to be used as reinforcing elements in cement based materials.

More adequate nanotubes to be used in the field of cementitious materials would reasonably be those that could be chemically more compatible with the main components of a cementations matrix, thus potentially providing a higher affinity for
15 the cementitious matrix and improved mechanical properties of the final product.

In theory, an example of such nanotubes could be nanotubes of portlandite and/or tobermorite. Portlandite is an oxide mineral, the naturally occurring form of calcium hydroxide, $\text{Ca}(\text{OH})_2$. It is a hydration product of Portland cement and the calcium analogue of brucite, $\text{Mg}(\text{OH})_2$.

20 Tobermorite is a calcium silicate hydrate mineral. Portlandite and tobermorite are inorganic layered compounds and nanotubes of these materials are not known to date.

Recent atomistic simulations have shown chances that portlandite nanotubes could in theory exist since the bending energy required for their formation is equivalent to
25 the one found in other existing inorganic nanotubes such as $\text{Mg}(\text{OH})_2$ and carbon nanotubes, see H. Manzano *et al.*, Advanced Materials 24 (24), 3239-3245, 2012. However, apart from the above theories, to date, as mentioned, no synthesis of portlandite nanotubes has been described and no reports of naturally occurring portlandite nanotubes have been found either.

In the existing literature, the preparation of different tubular inorganic materials such as metal dichalcogenides, halides, oxides and hydroxides can be found. Among hydroxides, the synthesis of $\text{Mg}(\text{OH})_2$ nanotubes have also been reported, see for example W. Fan et al., J. Mat. Chem. 13, 3062-3065, 2003. Since magnesium
5 belongs to the same group of the periodic table as calcium, they share certain chemical trends so that, a synthetic route used to obtain the $\text{Mg}(\text{OH})_2$ nanotubes could be, in theory, used by analogy as a model to obtain calcium hydroxide nanotubes.

However, it has to be underlined that due to its chemical-physical characteristics the
10 calcium ion does not completely behave as the magnesium ion does and so such analogous reactions might not have a similar outcome. It is known that, compared to magnesium, calcium (as well as strontium and barium) shows a higher reactivity and ligand exchange. Also, in the case of the hydroxide compounds, calcium hydroxide is a stronger base than magnesium hydroxide, soluble in water whilst
15 $\text{Mg}(\text{OH})_2$ is insoluble. $\text{Ca}(\text{OH})_2$ reacts quite readily with CO_2 to give CaCO_3 , whereas $\text{Mg}(\text{OH})_2$ is quite stable towards carbonation. In fact, the following publications concerning the synthesis of calcium carbonate nanotubes for biological applications, namely drug delivery, can be mentioned: H. Sugihara et al. Materials Letters 63, 322-324, 2009; J. Tang et al. Biol. Trace Elem. Res. 147, 408-417, 2012.

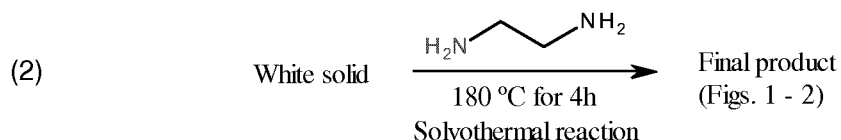
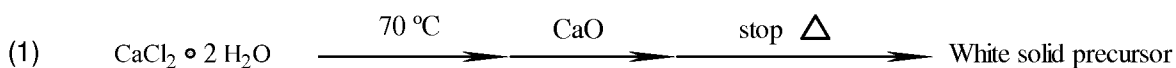
20 However, as said, no reports on portlandite nanotubes can be found to date.

The aforementioned W. Fan et al. synthesized $\text{Mg}(\text{OH})_2$ nanotubes through a precursor, i.e. $\text{Mg}_{10}(\text{OH})_{18}\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ nanowires obtained by reacting a magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) solution with magnesium oxide. The precursor, or intermediate, was then filtered, washed and dried, and afterwards placed in a
25 autoclave with ethylenediamine as a solvent to undergo a solvothermal reaction, carried out at 180°C for 6 hours. After completion of the solvothermal reaction the above-mentioned magnesium hydroxide nanotubes were obtained. The authors suggest that the formation of such $\text{Mg}(\text{OH})_2$ nanotubes is due to two factors, the first one being the wire-like morphology of the $\text{Mg}_{10}(\text{OH})_{18}\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ precursor, and the
30 second one the use of the ethylenediamine coordinating bidentate ligand which is believed to play a key role in the mechanism of the formation of the $\text{Mg}(\text{OH})_2$ nanotubes.

Also L. Zhuo et al., Crystal growth and design, 9 (1), 1-6, 2009, describe a solvothermal synthesis of $\text{Mg}(\text{OH})_2$ nanotubes carried out in autoclave, where again intermediates need to be isolated, and washing and centrifugation steps to be repeated several times (5 to 7 times) are required before carrying out the solvothermal reaction in water/methanol 1:1 solution

When first trying to develop a possible synthetic route for $\text{Ca}(\text{OH})_2$ nanotubes according to the purposes of the present invention, as a first attempt a similar reaction to the model proposed in the aforementioned W. Fan et al. was carried out, aiming at possibly producing $\text{Ca}(\text{OH})_2$ nanotubes instead of $\text{Mg}(\text{OH})_2$ through an analogous route. Thus, by firstly reacting calcium chloride dihydrate (instead of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) with CaO (instead of MgO), a white solid precursor, or intermediate, was obtained; it was filtered, washed and dried, and afterwards placed in a autoclave with ethylenediamine as a solvent to subject it to a solvothermal reaction.

The process is summarised by the following reaction schemes 1 and 2.

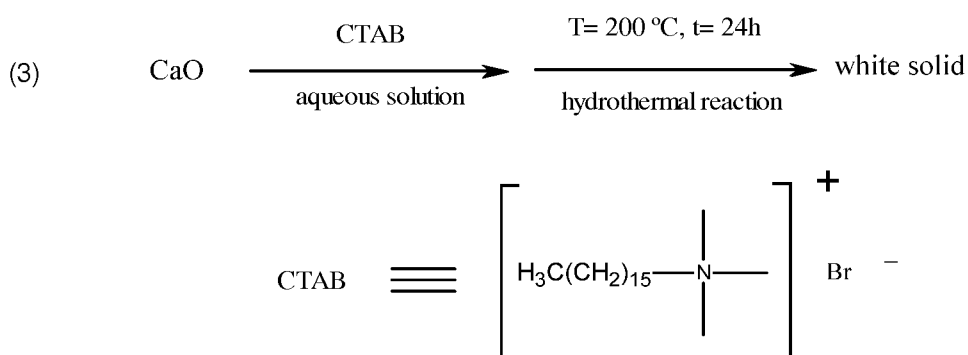


The final product was a mixture including calcium carbonate as well as some $\text{Ca}(\text{OH})_2$. The water used was decarbonated. In comparative Figure 1 of the enclosed drawings, the X-ray diffractogram (XRD) is shown of the final solid obtained in the above reaction scheme 2 after the solvothermal treatment. The peaks observed in the diffractogram can be ascribed to the following compounds: calcite (JCPDS 01-072-1937), vaterite (JCPDS 00-024-0030), aragonite (JCPDS 00-041-1475), three different minerals of CaCO_3 and calcium hydroxide (JCPDS 01-084-1267). (JCPDS: Joint Committee on Powder Diffraction Standards).

However, even though some $\text{Ca}(\text{OH})_2$ can be determined by diffraction as shown in Fig. 1, when characterizing the morphology of the same final product by TEM (JEOL JEM-1230 at 120 kV), the enclosed comparative Figure 2 shows that neither nanotubes could be detected, nor any type of fibre-like shapes or morphologies could be observed.

H. Dhaouadi et al., Nano-Micro Letters 3(3), 153-159, 2011 describes a further method to obtain $\text{Mg}(\text{OH})_2$ nano-rods, in this case by a hydrothermal reaction starting from MgO powder dispersed in aqueous solution in the presence of cetyltrimethylammonium bromide (CTAB) as surfactant. The reference reports that surfactants are used to prepare metal oxide nanoparticles in which the polar groups directly interact with the particles surface and strongly influence the shape. CTAB is a cationic surfactant which can be adsorbed on the surface of $\text{Mg}(\text{OH})_2$ and act as a directing agent by the interaction of positively charged head groups (CTA^+) with hydroxyl groups (O-H).

Therefore, again when trying to develop from such reaction a model for a possible synthetic route of $\text{Ca}(\text{OH})_2$ nanotubes according to the purposes of the present invention, as a further attempt a corresponding synthetic route was adapted therefrom according to the following reaction scheme 3:



In this case a mixture of calcium hydroxide and calcium carbonate was obtained and characterized by XRD, but when the morphology of the mixture was analysed by TEM (JEOL JEM-1230 at 120 kV), platelet-like and shapeless morphologies were shown in the TEM evidence of the enclosed comparative Figure 3. Therefore the

morphologies obtained were not even fibre-like or rod-like, not to mention nanotube-like as exactly aimed at according to the purposes of the present invention.

Also an attempt according to the purposes of the present invention to repeat the process as proposed by the aforementioned L. Zhuo et al. by replacing the raw material MgCl_2 with CaCl_2 proved to be unsuccessful, since no useful intermediate could be formed.

The above evidence further confirmed that, within the scope of the technical problem faced by the present invention, calcium does not behave the same way as magnesium so that the background art relating to $\text{Mg}(\text{OH})_2$ nanotubes turns out to be an essentially useless model in the attempts to provide $\text{Ca}(\text{OH})_2$ nanotubes with satisfying properties according to the purpose of the present invention.

To such purpose, thus a different synthetic route has to be conceived.

BRIEF DESCRIPTION OF THE INVENTION

According to the present invention, portlandite nanotubes are obtained by a process comprising the following steps:

- a) reacting calcium chloride with calcium oxide in aqueous solution, thus obtaining an aqueous dispersion;
- b) feeding as such the aqueous dispersion obtained in step a) to a hydrothermal reaction, thus obtaining portlandite nanotubes.

The invention also concerns the use of the said portlandite nanotubes as a component for cementitious compositions, particularly as a reinforcing material to provide cementitious products with improved mechanical properties, especially resistance under tensile stress.

The invention also concerns the said cementitious compositions and final products obtained therefrom, which comprise the said portlandite nanotubes as a component, particularly as a reinforcing material. In particular, it refers to cementitious compositions comprising at least a hydraulic binder and aggregates for the production of mortars or concrete, comprising the aforementioned portlandite nanotubes.

DETAILED DESCRIPTION OF THE INVENTION

In a preferred embodiment, portlandite nanotubes are obtained by carrying out step a) as follows: a $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (calcium chloride dihydrate) aqueous solution is heated at a moderate temperature, between 40°C and 100°C , more particularly between 60°C and 80°C and solid CaO is then added to the heated solution and stirred for a time of at least 5 minutes. When the addition of CaO is completed, heating is stopped and the obtained dispersion is left to cool and react at room temperature for a longer time, at least 24 hours.

Preferably CaO is added to the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (calcium chloride dihydrate) aqueous solution in an amount according to a molar ratio $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}/\text{CaO}$ which varies approximately between 1:1 to 10:1, respectively, and preferably between 1:1 to 5:1, respectively.

After completion of step a), without any previous treatment such as filtering or washing, the dispersion is then subjected to step b) by directly feeding it as such into a reactor for the hydrothermal reaction according to step b).

The hydrothermal reaction is carried out by heating the dispersion at a temperature preferably in a range between 160°C and 270°C , more particularly between 180°C and 270°C for a time of at least 4 hours. The final solid thus obtained is filtered and rinsed with water.

The thus obtained solid is portlandite with nanotube structure, defined by characterisation mainly based on X-ray diffraction (XRD), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). The nanotube structure of the fibre can be further confirmed by extracting electron density profiles from the TEM images, for example from a specific area delimited on the TEM image. The electron density profile shows the intensity of the electrons that pass through the analysed material. When the intensity is high, or relatively high, it means that there is no material, so no transit of electrons through any material, or that there is an electron transit through a very thin layer of material. Conversely, when the intensity is low or approaching zero, it means that the material is quite compact so that the electrons are not able to transit through the material. The electron density profile of the nanotube shows a high intensity outside the tube,

which lowers to nearly zero (the electrons do not pass through the walls of the nanotube formed by layers of $\text{Ca}(\text{OH})_2$), and then increases to a certain extent in the middle of the tube, which indicates that the electrons pass through a thinner layer of material as would be in case of a hollow tube.

- 5 Furthermore, from the electron density profile the inner diameter of the nanotube can also be measured.

DESCRIPTION OF THE DRAWINGS

- As described above, Figures 1 to 3 of the enclosed drawings show X-ray diffractogram, XRD (Fig. 1) and transmission electron microscopy (TEM) images (Figs. 2 and 3) of reference products made for comparative purposes and falling outside the scope of the present invention.

Figure 4 and Figure 11 show X-ray diffractograms, XRD, of samples as obtained in the following Examples 1 and 2, respectively, according to the invention.

- 15 Figures 5 and 6 show transmission electron microscopy (TEM) images of the sample as obtained in the following Example 1 according to the invention.

Figure 7 shows an electron density profile of the sample of Fig. 6.

- Figures 8 and 9 show a high-resolution transmission electron microscopy (HRTEM) image of the sample as obtained in the following Example 1 according to the invention.

Figure 10 shows an electron density profile of the sample of Fig. 9.

Figure 12 shows a transmission electron microscopy (TEM) image of the sample as obtained in the following Example 2 according to the invention.

Figure 13 shows an enlargement of Fig. 12.

- 25 Figure 14 shows an electron density profile of the sample obtained in the same Example 2.

Figure 15 and Figure 19 show X-ray diffractograms, XRD, of samples as obtained in the following Examples 3 and 4, respectively, according to the invention.

Figures 16 and 17 show a transmission electron microscopy (TEM) image of the sample as obtained in the following Example 3 according to the invention.

- 5 Figures 20 and 21 show a transmission electron microscopy (TEM) image of the sample as obtained in the following Example 4 according to the invention.

Figure 18 shows an electron density profile of the sample of Fig. 17.

Figure 22 shows an electron density profile of the sample of Fig. 21.

EXAMPLES

- 10 The following examples illustrate the invention without in any way limiting the scope thereof. The characterisation of the final product obtained in the examples was carried out by X-ray diffraction (XRD), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) as follows. The X-ray diffraction measurements were made by a Philips X'Pert Pro MPD pw3040/60,
15 equipped with a copper ceramic tube and employing a continuous scanning in the 2θ range from 2° to 75° , and a generator power of 40 kV and 40 mA.

- The final products were then characterised by a JEOL JEM-1230 thermionic emission transmission electron microscopy (120kV) with a digital camera and some of the samples were also observed on a JEM-2200 FS/CR (JEOL, Ltd.) field
20 emission gun (FEG) transmission electron microscopy operated at 200 kV. The samples were dispersed in acetone and a drop of the dispersion was applied to a carbon grid.

EXAMPLE 1

- 3 M aqueous solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is prepared. While heating the solution at 70°C ,
25 solid CaO is added and stirred for 10 minutes. The mixture is left reacting for 68 hours, at room temperature. Then the so obtained dispersion is directly fed as such, without filtering or washing, to a reactor and heated to 200°C . The hydrothermal

reaction is carried out for 15 hours. The solid obtained is filtered and rinsed with water.

The final solid was characterized by X-ray diffraction as shown in the enclosed Figure 4. The XRD pattern of the solid is ascribed to the hexagonal phase of $\text{Ca}(\text{OH})_2$ (JCPDS 01-084-1271).

The solid was also analysed by transmission electron microscopy (JEOL JEM-1230 at 120 kV), scale bar 0.2 μm , see Fig. 5. The product obtained shows fibre-like/rod-like morphologies of micrometres in length and diameters between 23 nm and 44 nm. At higher magnification (scale bar 50 nm), see Fig. 6, a nanotube morphology can clearly be defined, as indicated by the arrows.

The nanotube nature of the fibre can be further confirmed by extracting electron density profiles from the TEM images, see Fig. 7, which shows the electron density profile extracted from the area delimited by the box traced on the image of Fig. 6. The ordinate refers to counts and the abscissa to d , measured as nm.

As mentioned above, the electron density profile shows the intensity of the electrons that pass through the analysed material. When the intensity is high or relatively high, it means that the electrons do not go through any material or they go through a very thin layer of material. When the intensity is very low or almost zero, it means that the electrons are not able to go through the material which indicates that the material is quite compact. The electron density profile of the nanotube shows a high intensity outside the tube, which lowers to nearly zero where the electrons do not go through the walls of the nanotube formed by layers of $\text{Ca}(\text{OH})_2$, and then increases in the middle of the tube to a certain extent, which indicates that the electrons there pass through a thinner layer of material, as in the case of a hollow tube. Furthermore, from the electron density profile, the inner diameter of the nanotube can also be measured, which turns out to be around 42 nm in the case of the example at issue.

The product obtained in Example 1 was then analysed by high resolution transmission electron microscopy, HRTEM (JEOL JEM-2200 FS/CR operated at 200 kV). In figure 8 a $\text{Ca}(\text{OH})_2$ nanotube is shown at high resolution (indicated by

the arrows). In the image of Fig. 8 the different layers that form the wall of the nanotube can be seen, clearly showing its multiwalled nature. The inner diameter of the nanotube is 8.8 nm.

Figure 9 is an enlargement of Fig. 8, where a specific area is delimited by a box, again for electron density profile purpose. The corresponding electron density profile as obtained from that traced box is shown in Figure 10. The ordinate refers to counts and the abscissa to d , measured as nm.

EXAMPLE 2

To a 3 M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ aqueous solution kept at 70°C, solid CaO is added and stirred for 30 minutes and the dispersion is left reacting for 44 hours at room temperature. Then the so obtained dispersion, without previous filtering or washing, is fed as such to a reactor and heated to a temperature of 250 °C. The reaction is carried out for 15 hours. The solid thus obtained is filtered and rinsed with water.

The solid was characterized by X-ray diffraction, see Fig. 11. Apart from a set of peaks of low intensity which can be assigned to the rhombohedral phase of calcium carbonate (JCPDS 01-081-2027), possibly formed due to a small quantity of CO_2 unremoved from the water, the main peaks obtained can be ascribed to the hexagonal phase of $\text{Ca}(\text{OH})_2$ (JCPDS 01-084-1265).

The product obtained from Example 2 was also characterized by transmission electron microscopy (JEOL JEM-1230 at 120 kV), see Fig. 12, scale bar 0.2 μm , and the enlargement of Fig. 13, scale bar 100 nm. TEM images show that fibre-like morphologies of portlandite were formed in the synthesis, as well as nanotube particles shown in Fig. 13 and marked with arrows, scale bar 100 nm. The diameter of the fibres or nanotubes of Example 2 ranges between 17 nm and 44 nm.

As shown in Fig. 14, the electron density profile is reported with reference to the area marked by a box on the nanotube of Fig. 13. The ordinate refers to counts and the abscissa to d , measured as nm. The electron density profile of the marked area confirms the nanotube structure at issue. The inner diameter of the nanotube is 29.84 nm.

EXAMPLE 3

Whilst in example 1 and example 2 above CaO is added to said solution according to a molar ratio $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ to $\text{CaO} = 10/1$ respectively, a lower molar ratio $\text{CaCl}_2 \cdot 2\text{H}_2\text{O} / \text{CaO} = 5/1$ is used in the present example as follows.

- 5 To a 3M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution at 70°C, solid CaO is added according to a molar ratio $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ to $\text{CaO} = 5/1$ in 30 minutes and left reacting for 72 hours at room temperature.

Then the so obtained dispersion is directly fed as such, without filtering or washing, to a reactor and heated to 200 °C. The hydrothermal reaction is carried out for 15
10 hours. The solid obtained is filtered, rinsed with water and washed with absolute ethanol.

The final solid is characterized by X-ray diffraction, see Fig. 15. The obtained sample is mainly made of calcium hydroxide and some calcium carbonate. A set of peaks is visible to be assigned to the rhombohedral phase of calcium carbonate (JCPDS
15 00-001-0837), possibly formed due to a small quantity of unremoved CO_2 . The remaining peaks are to be ascribed to the hexagonal phase of $\text{Ca}(\text{OH})_2$ (JCPDS 01-084-1263).

The product obtained was also characterized by transmission electron microscopy (TEM) (JEOL JEM-1230 at 120 kV), see Fig 16, scale bar 200 nm. Fibre-like
20 morphologies were obtained as shown in Fig. 16, as well as nanotube particles as shown in figure 17 in which one of the fibres, indicated by the arrows, is shown to be shaped like a nanotube.

The nanotube structure is also confirmed by the corresponding electron density profile which is shown in Fig. 18. The electron density profile indicates that the
25 diameter of the nanotube of Fig. 17 is 134 nm.

EXAMPLE 4

An even lower molar ratio $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ to $\text{CaO} = 1/1$ is used in the present example.

To a 3M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution kept at 70°C , solid CaO according to a $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}/\text{CaO}$ ratio of 1/1 is added in 30 minutes and left reacting for 72 hours at room temperature.

Then the so obtained dispersion is directly fed as such, without filtering or washing,
5 to a reactor and heated to 200°C . The hydrothermal reaction is carried out for 15 hours. The solid obtained is filtered, rinsed with water and washed with absolute ethanol.

The final solid was characterized by X-ray diffraction, see Fig. 19. The sample was mostly made of portlandite and calcium carbonate, probably formed due to the CO_2
10 that was redissolved in water during the hydrothermal reaction. Some CaClOH was also present in the sample.

The X-ray spectrum shows that portlandite is present (hexagonal crystal system, JCPDS 00-044-1481, the peaks are marked with blue circles in Fig. 19), rhombohedral calcium carbonate (JCPDS 01-085-0849) and an impurity made of
15 CaClOH (JCPDS 00-036-0983) are also present.

The sample was analysed by transmission electron microscopy (JEOL JEM-1230 at 120 kV), see Fig. 20 showing a mixture of morphologies, that is, particle-like morphologies mixed with fibre-like morphologies.

When analysing further the fibre-like morphologies by TEM, the nanotube structure
20 of the fibres was confirmed according to Fig. 21, showing a TEM image of a nanotube-like morphology.

Fig. 22 shows the corresponding electron density profile which confirms the nanotube structure of the fibre. The inner diameter of that nanotube is 48.5 nm.

In conclusion, the present invention can finally accomplish the high-felt need of
25 providing portlandite with a nanotube structure, portlandite being a material highly compatible with a cementitious matrix. In particular, the portlandite nanotubes according to the present invention appear to be an ideal reinforcing component in cementitious compositions so as to provide final cementitious products, such as

mortars or concrete, with improved mechanical properties, such as improved resistance under tensile stress.

Moreover, portlandite nanotubes according to the present invention are a product-by-process where such process is substantially characterized by simple and straightforward steps, under mild operating conditions. In particular, no process intermediates need to be separated or isolated, and the whole process is carried out in aqueous solution, these being highly advantageous conditions for industrial scale-up.

CLAIMS

1) Portlandite nanotubes obtained by a process comprising the following steps:

a) reacting calcium chloride with calcium oxide in aqueous solution, thus obtaining
5 an aqueous dispersion;
b) feeding as such the aqueous dispersion obtained in step a) to a hydrothermal reaction, thus obtaining portlandite nanotubes.

2) Portlandite nanotubes according to claim 1 obtained by a process comprising the following steps:

10 a) heating a $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ aqueous solution at a temperature between 40°C and 100°C , adding solid CaO to the heated solution, letting the reaction run at room temperature;

b) feeding as such the aqueous dispersion obtained in step a) to the hydrothermal reaction, heating the dispersion at a temperature in a range between 160°C and
15 270°C , for a time of at least 4 hours, thus obtaining portlandite nanotubes.

3) Portlandite nanotubes according to claim 2 wherein in step a) solid CaO is added to the heated solution and stirred for a time of at least 5 minutes and the reaction is run at room temperature for a time of at least 24 hours.

4) Portlandite nanotubes according to claims 1 to 3 defined by characterisation
20 based on X-ray diffraction (XRD), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) as per the enclosed drawings.

5) Process for producing portlandite nanotubes, comprising the following steps:

a) reacting calcium chloride with calcium oxide in aqueous solution, thus obtaining
25 an aqueous dispersion;

b) feeding as such the aqueous dispersion obtained in step a) to a hydrothermal reaction, thus obtaining portlandite nanotubes.

6) Process according to claim 5 comprising the following steps:

a) heating a $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ aqueous solution at a temperature between 40°C and
30 100°C , adding solid CaO to the heated solution, letting the reaction run at room temperature;

b) feeding as such the aqueous dispersion obtained in step a) to the hydrothermal reaction, heating the dispersion at a temperature in a range between 160°C and 270°C for a time of at least 4 hours, thus obtaining portlandite nanotubes.

7) Process according to claim 6 wherein in step a) solid CaO is added to the heated solution, stirred for a time of at least 5 minutes and the reaction is run at room temperature for a time of at least 24 hours.

8) Process according to claim 6 wherein in step a) solid CaO is added to the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ aqueous solution in an amount according to a molar ratio $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ /CaO between 1:1 to 10:1, respectively.

9) Process according to claim 8 wherein in step a) solid CaO is added to the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ aqueous solution in an amount according to a molar ratio $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ /CaO between 1:1 to 5:1, respectively.

10) Process according to claims 5 to 9 wherein the portlandite nanotubes are defined by characterisation based on X-ray diffraction (XRD), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) as per the enclosed drawings.

11) Use of the portlandite nanotubes according to claims 1 to 4 as a component in cementitious compositions to provide mortars or concrete.

12) Use according to claim 11 as a reinforcing material in cementitious compositions.

13) A cementitious composition comprising an hydraulic binder and aggregates for the production of mortars or concrete, characterized in that it comprises portlandite nanotubes according to claims 1 to 4.

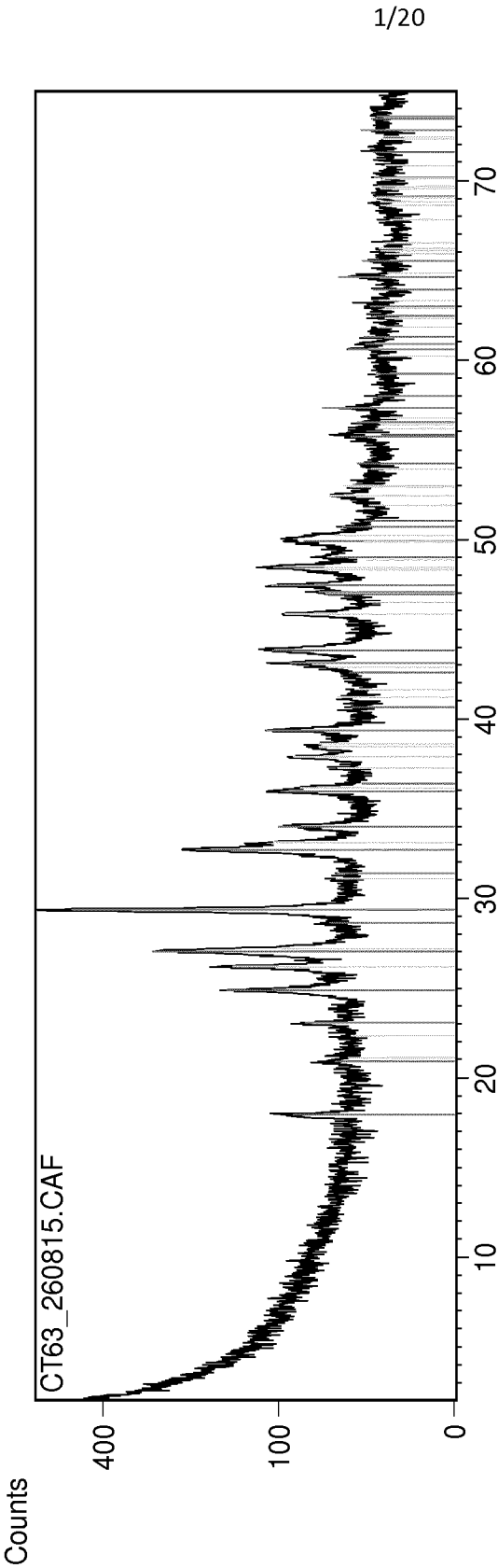


Fig. 1 (comparative)

Peak List	
01-072-1937; Ca C O3; Calcite	
00-024-0030; Ca C O3; Vaterite, syn	
00-041-1475; Ca C O3; Aragonite	
01-084-1267; Ca (O H)2; Calcium Hydroxide	

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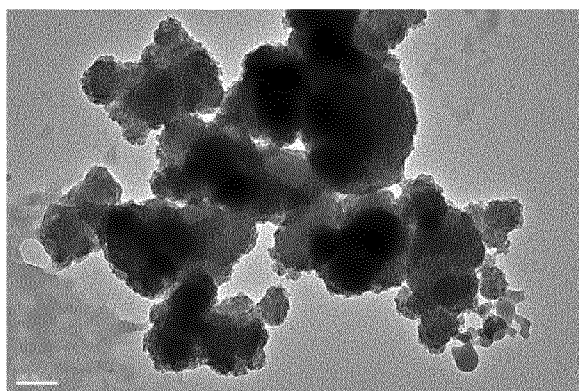
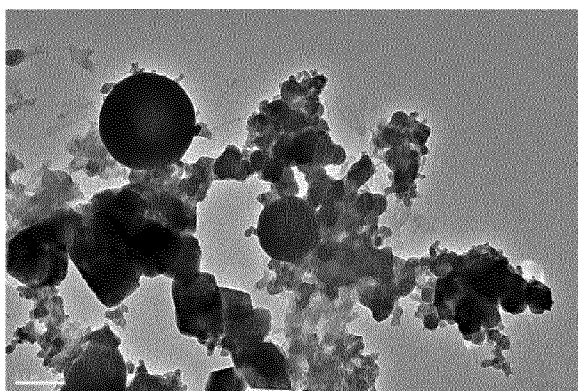
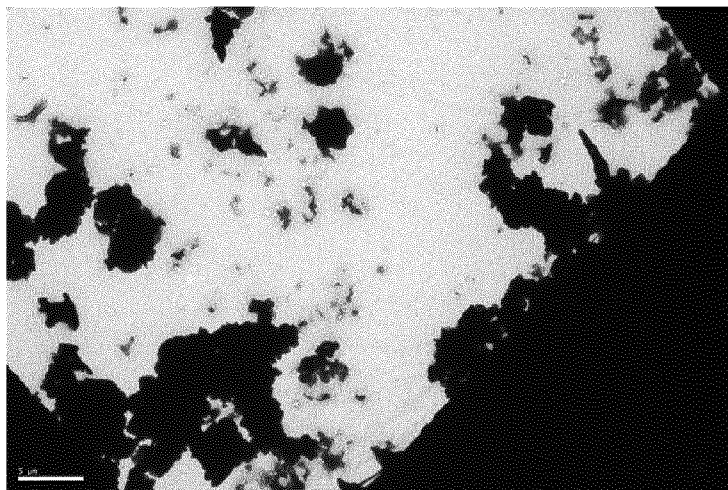


Fig. 2 (comparative)

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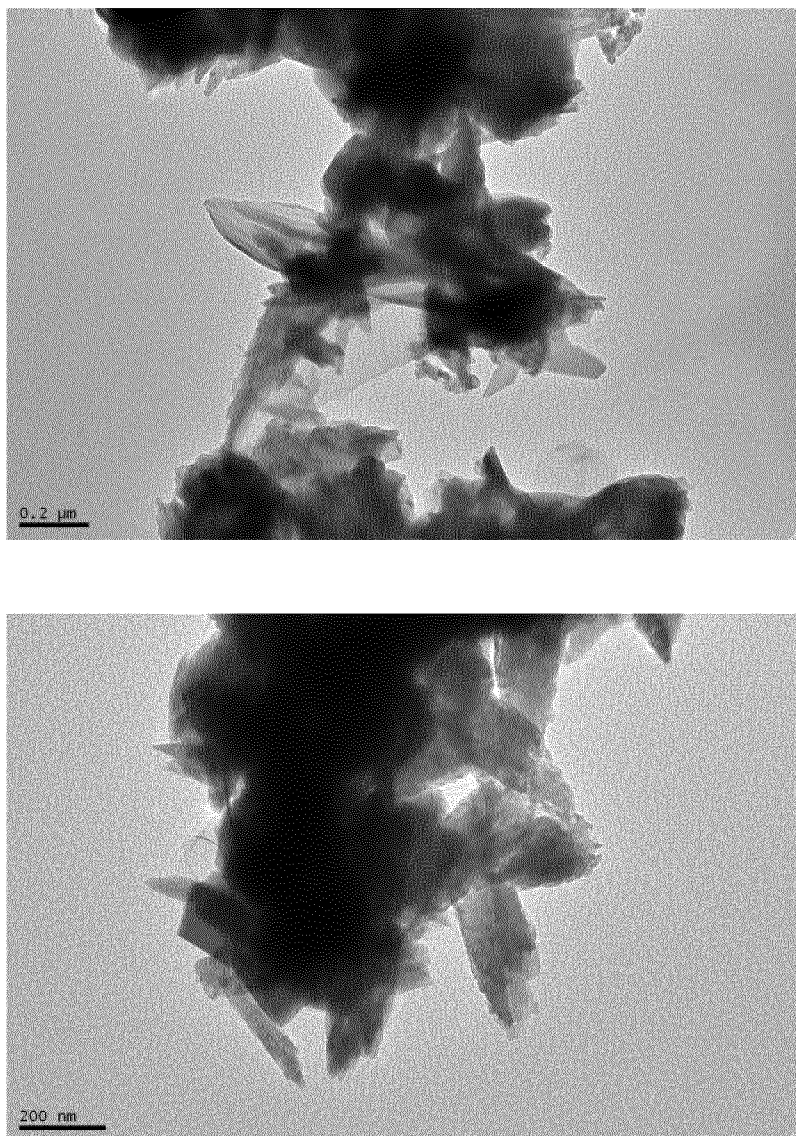


Fig. 3 (comparative)

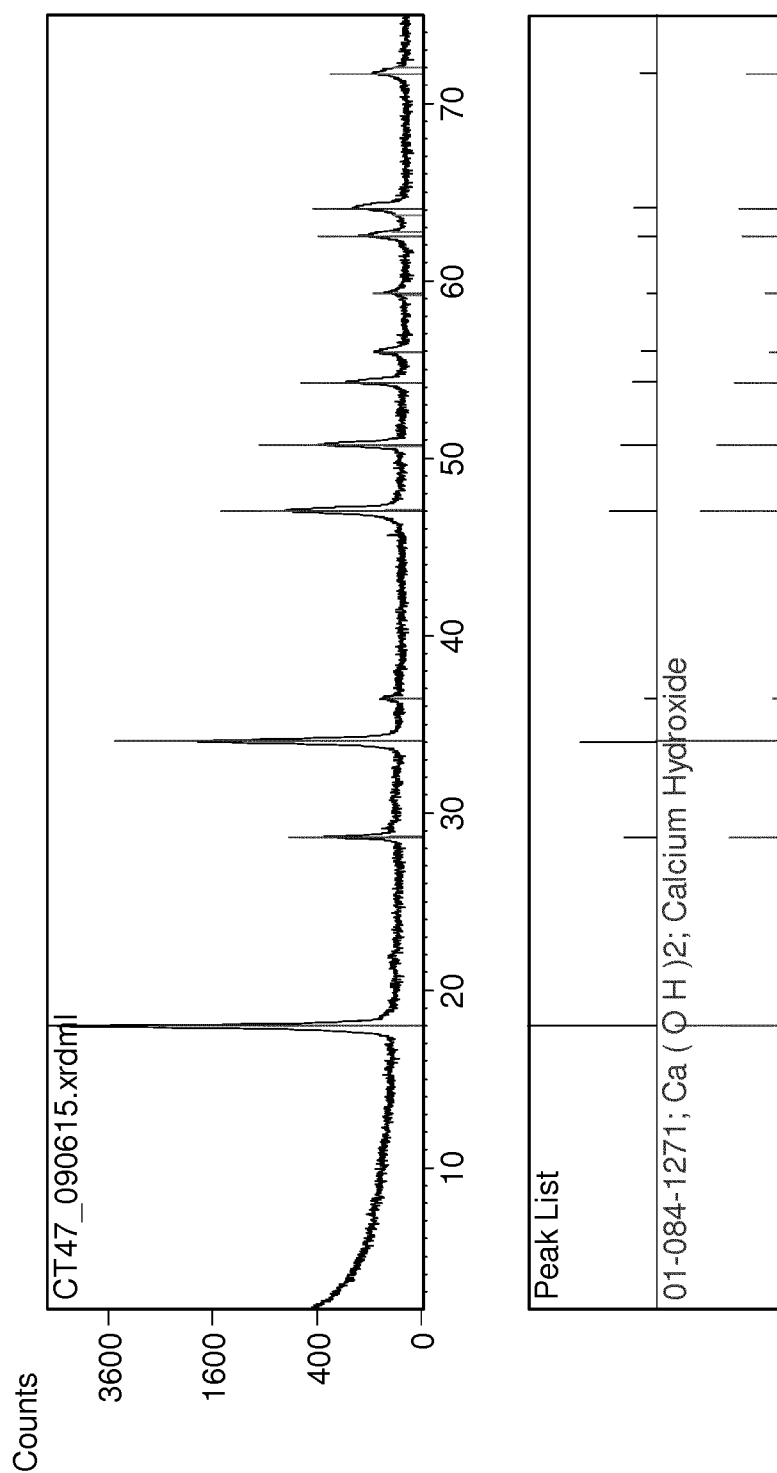


Fig. 4

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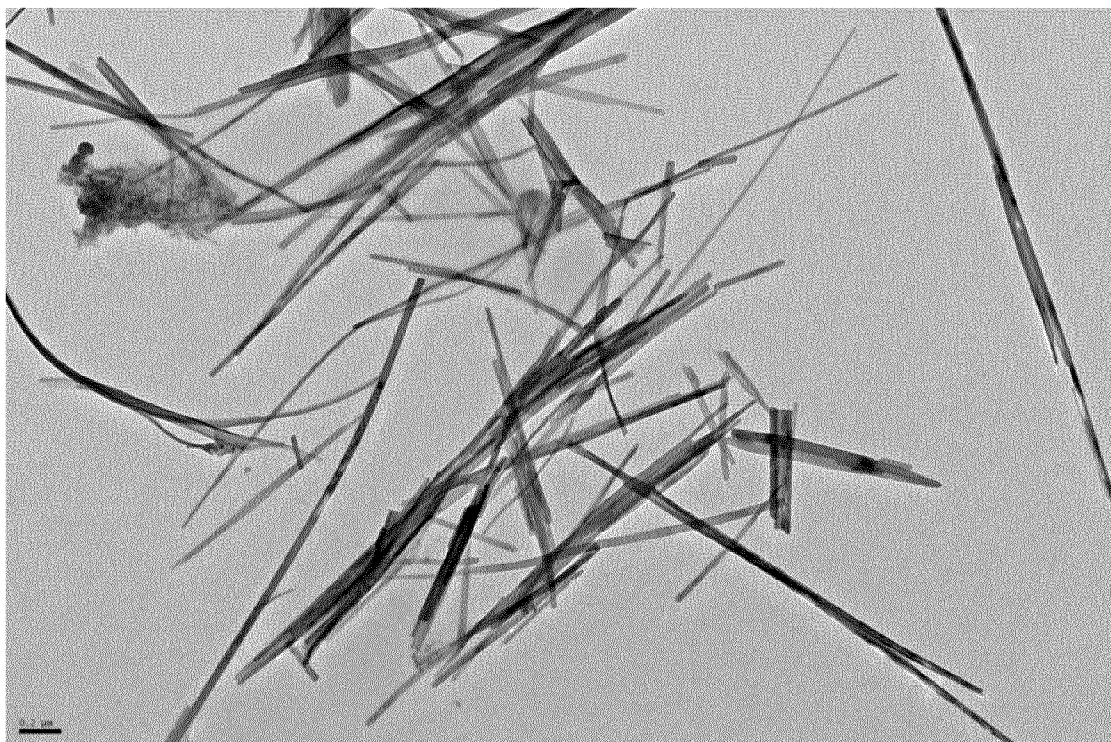


Fig. 5

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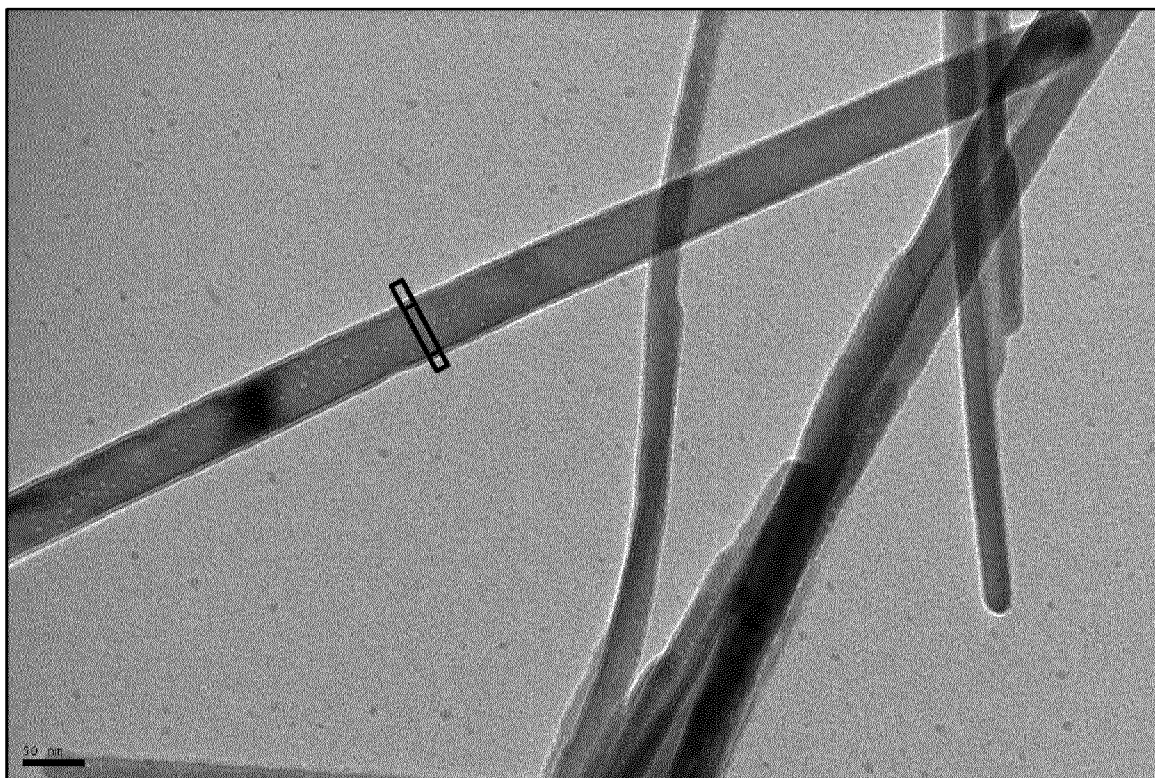
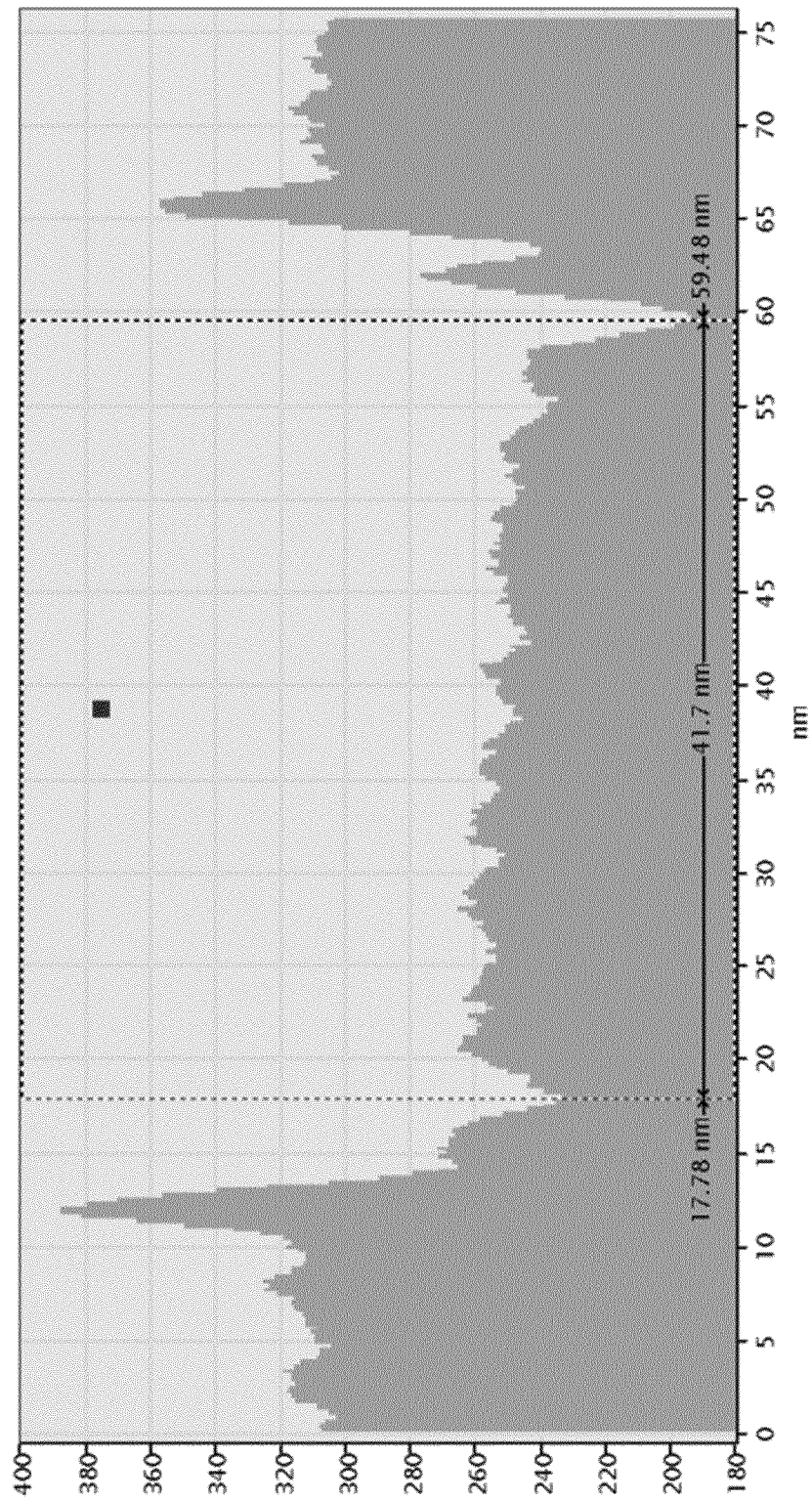


Fig. 6

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Fig. 7

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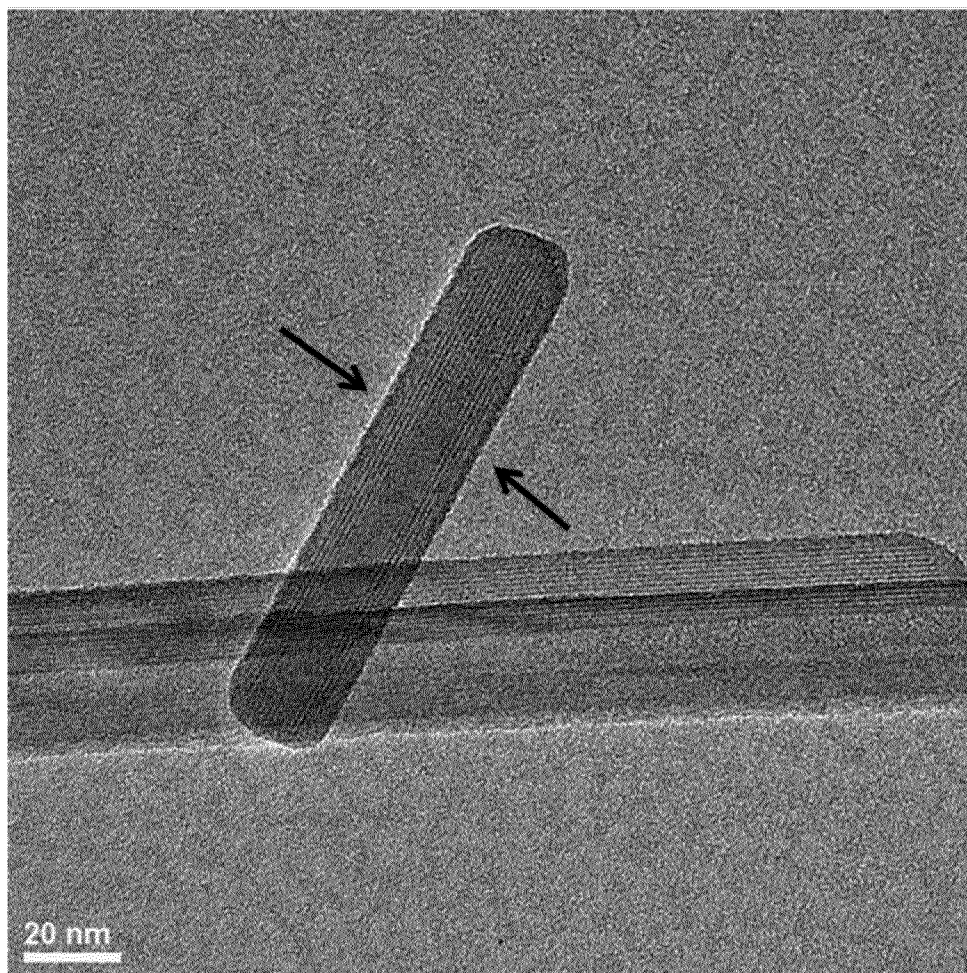


Fig. 8

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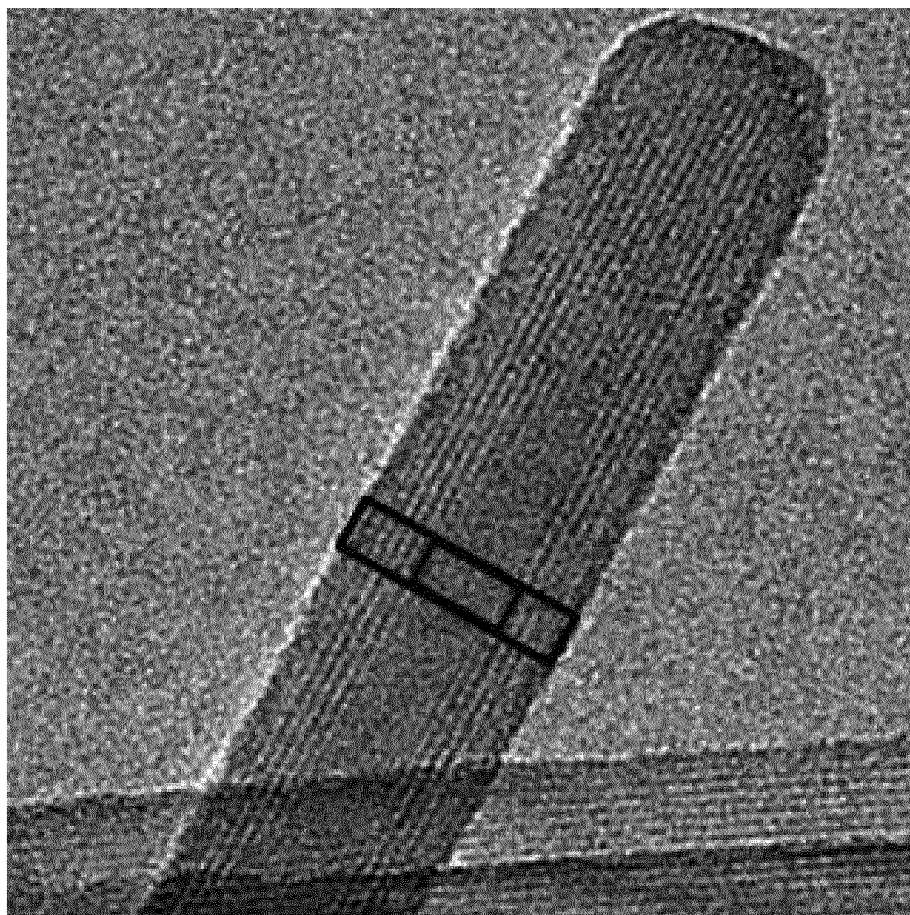
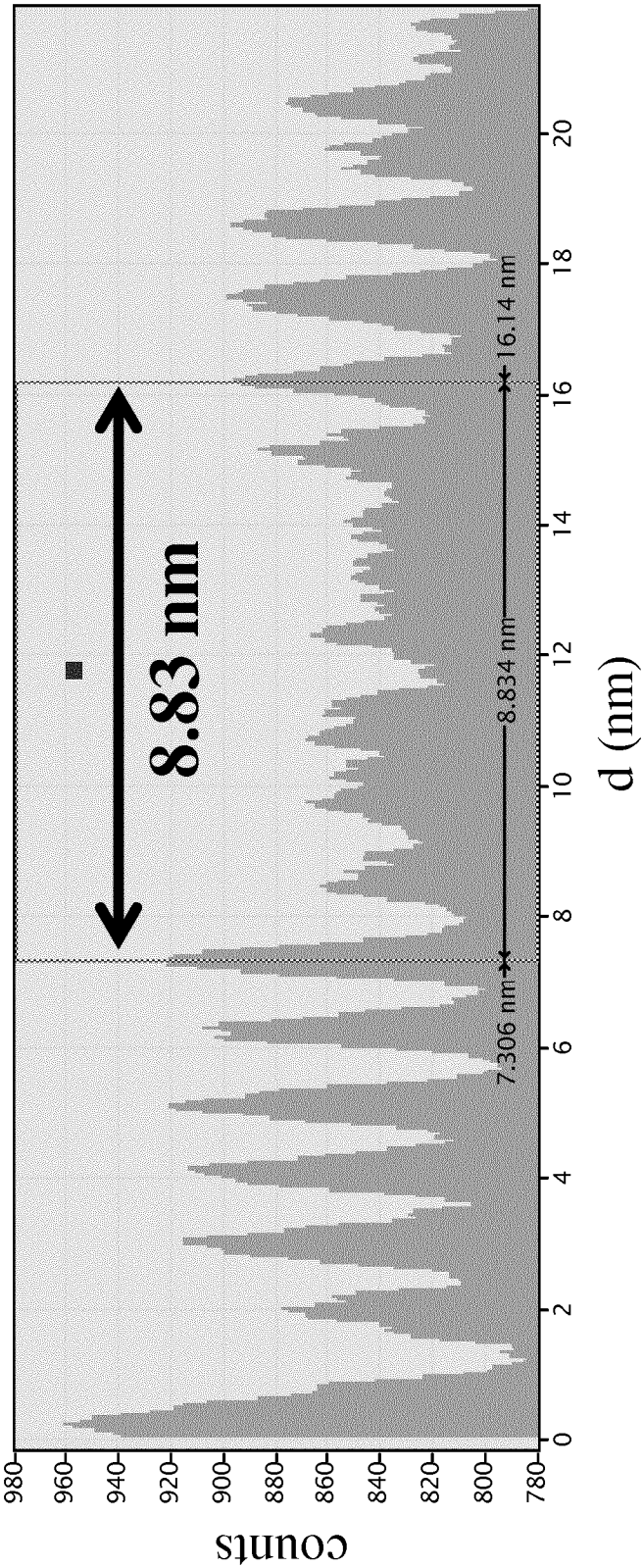


Fig. 9

Fig. 10



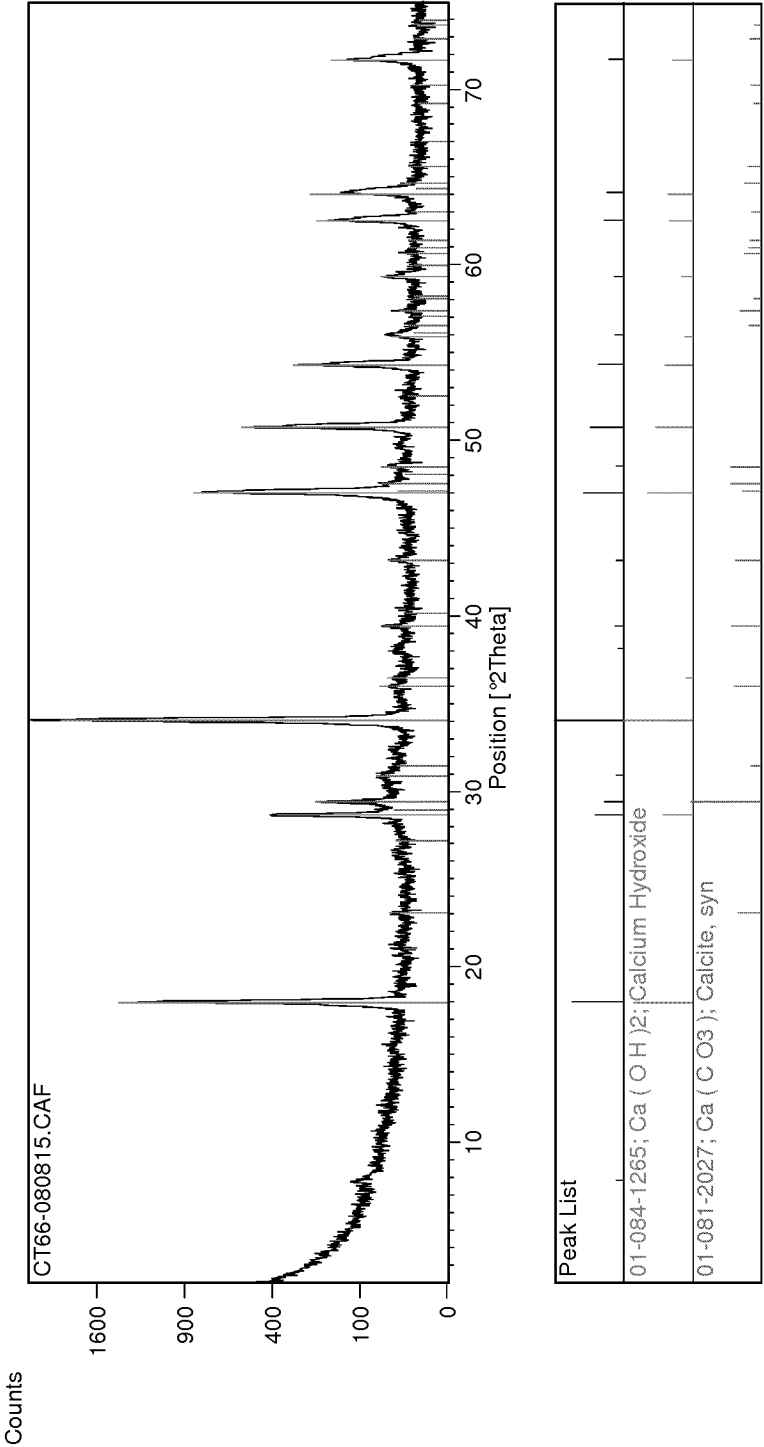


Fig. 11

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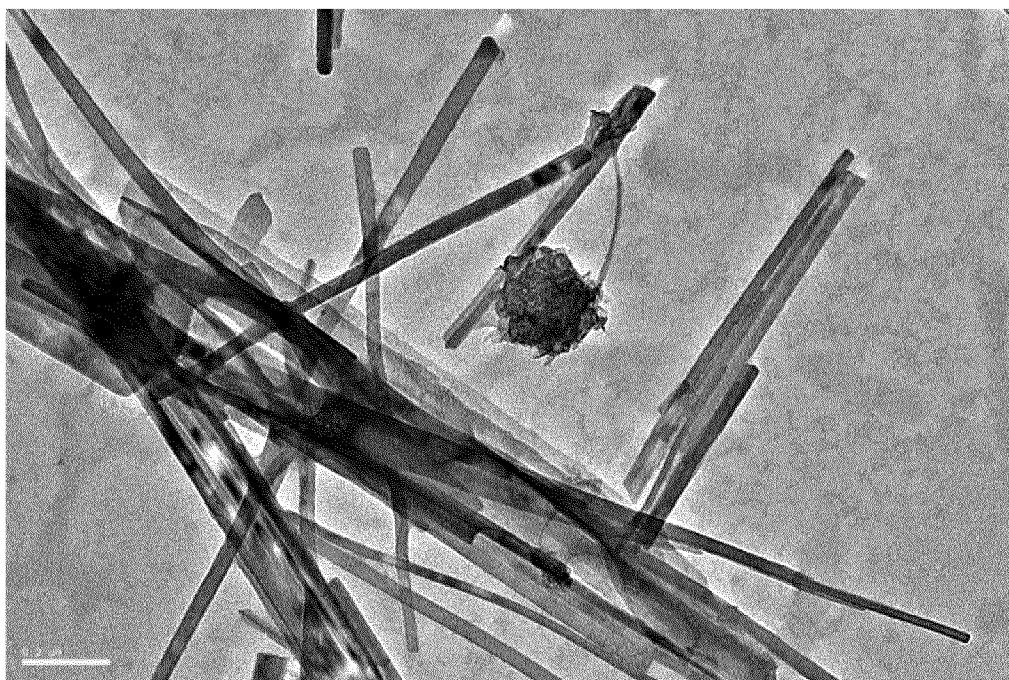


Fig. 12

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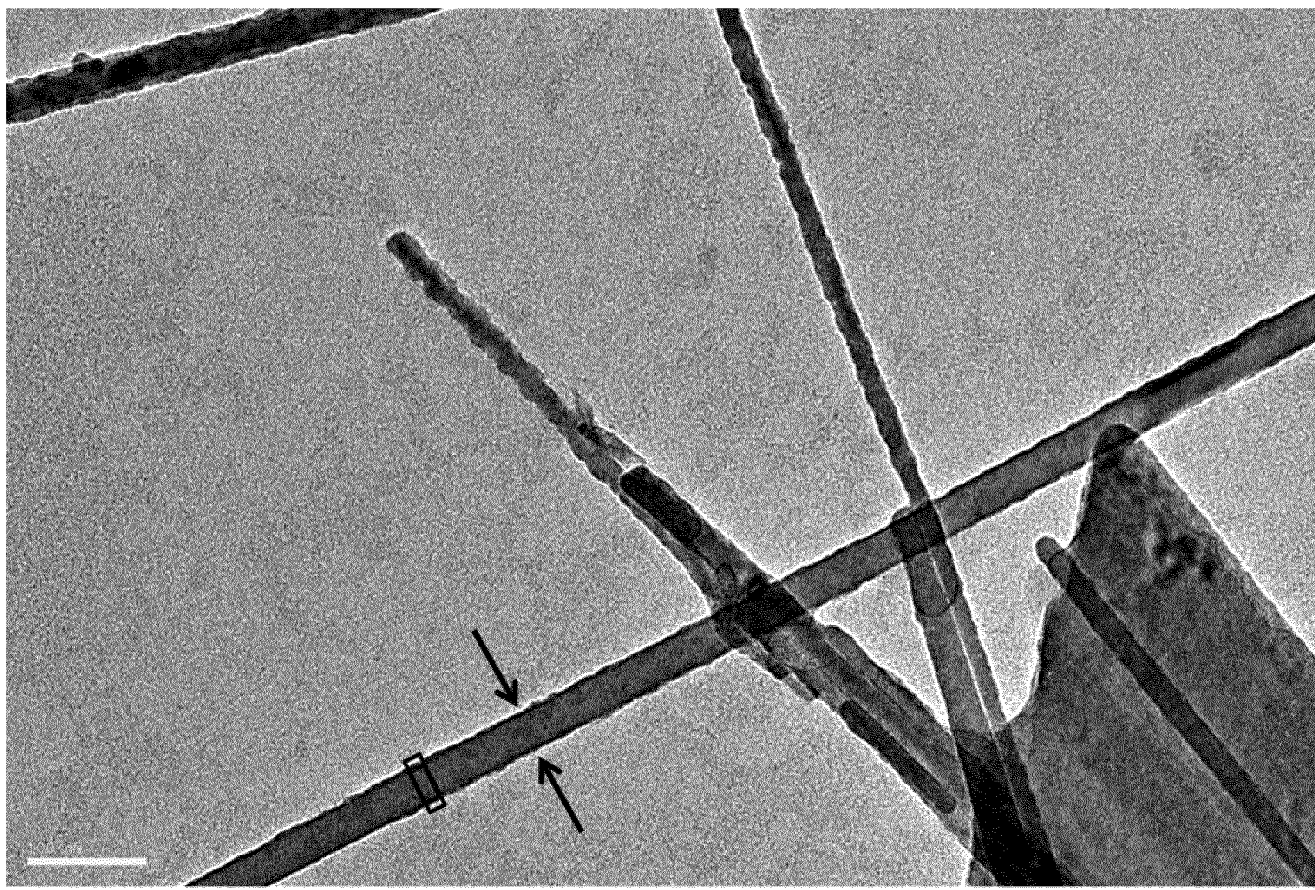


Fig. 13

Fig. 14

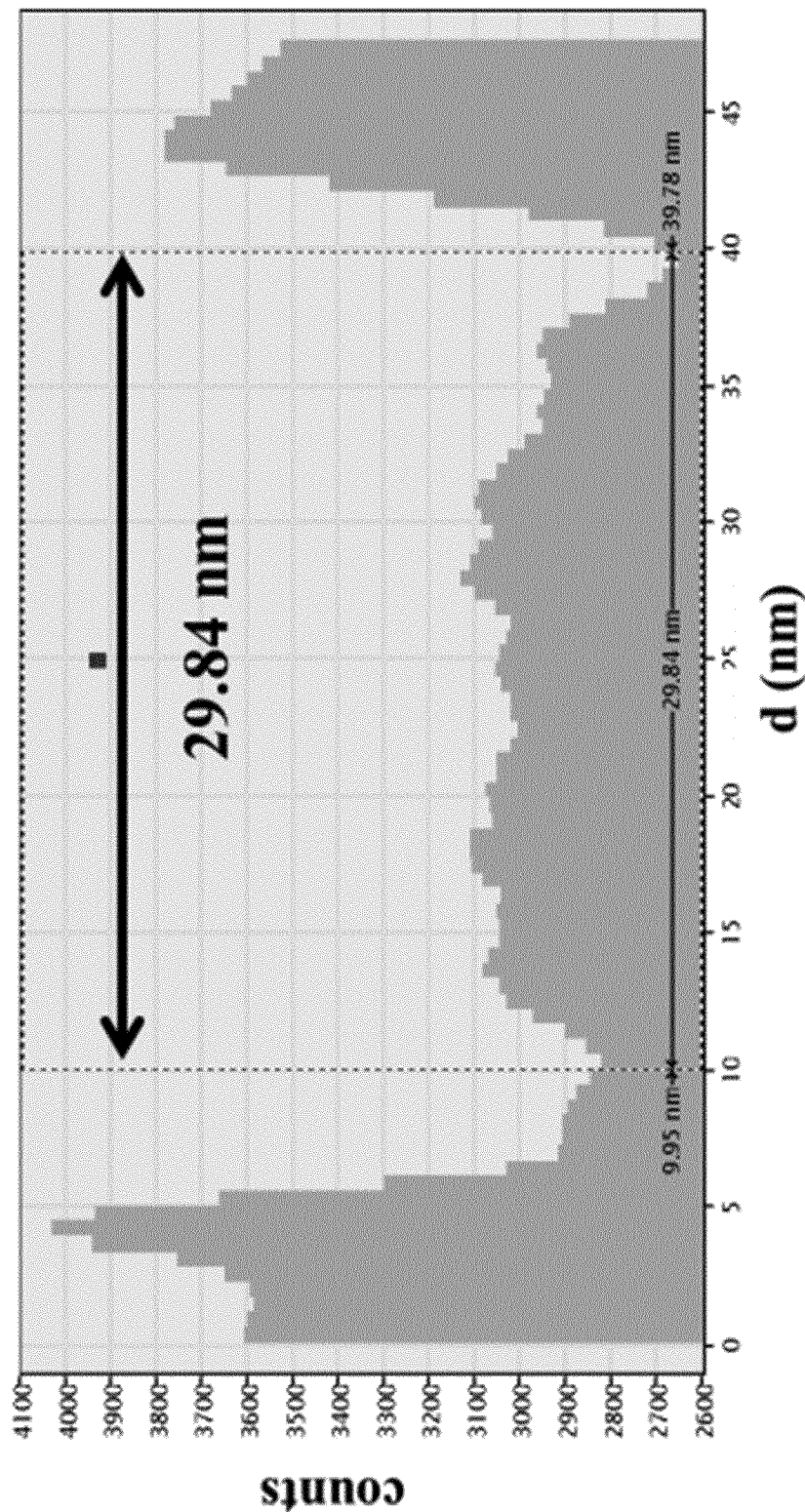
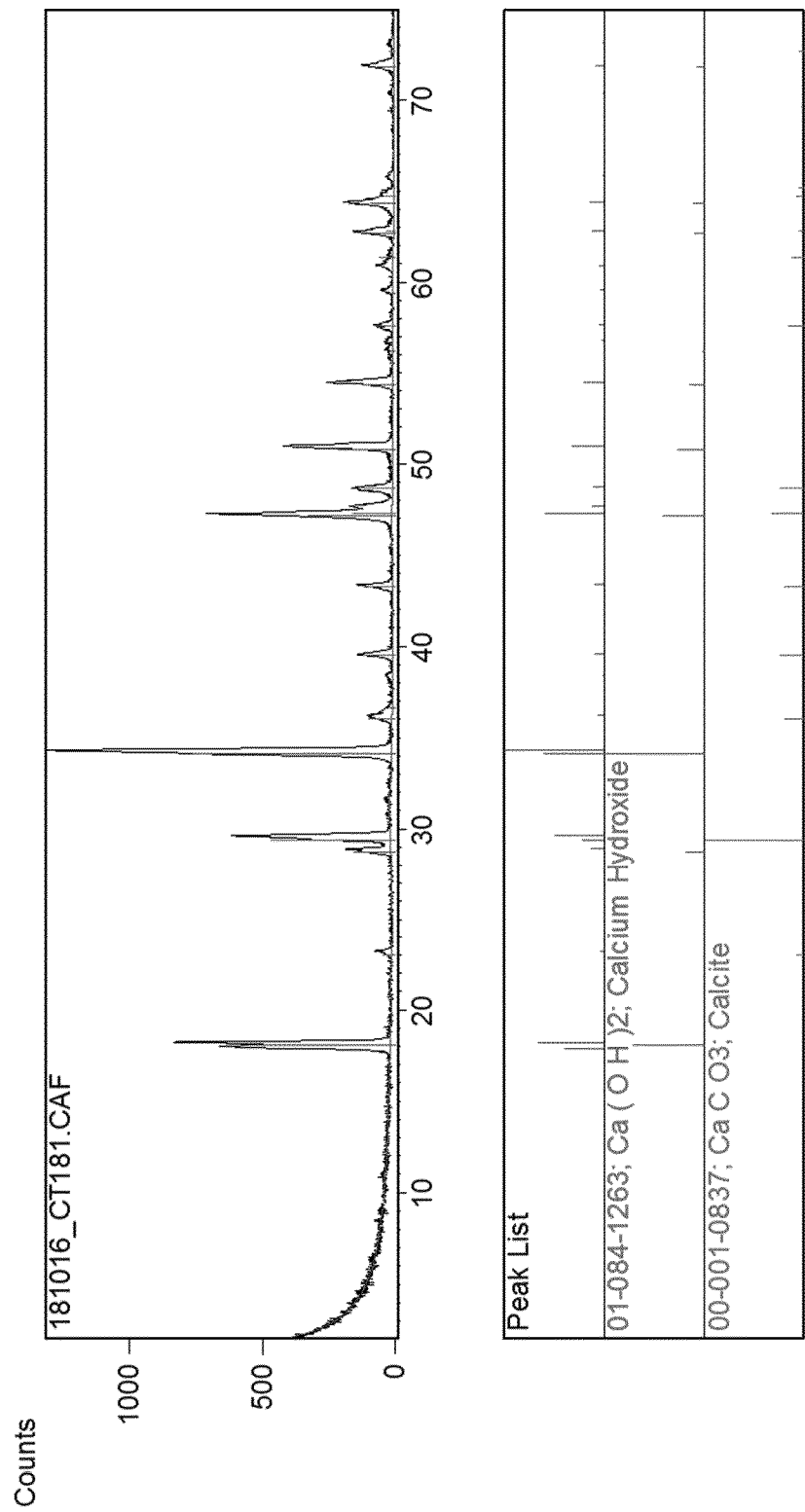


Fig. 15



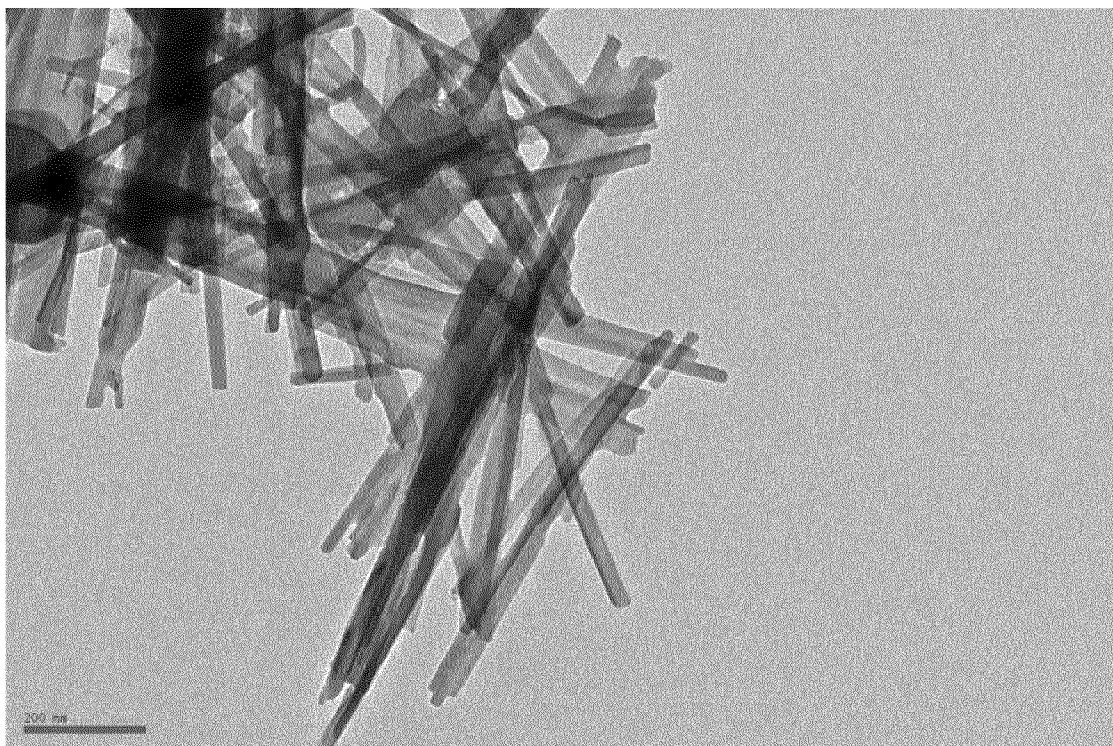


Fig. 16

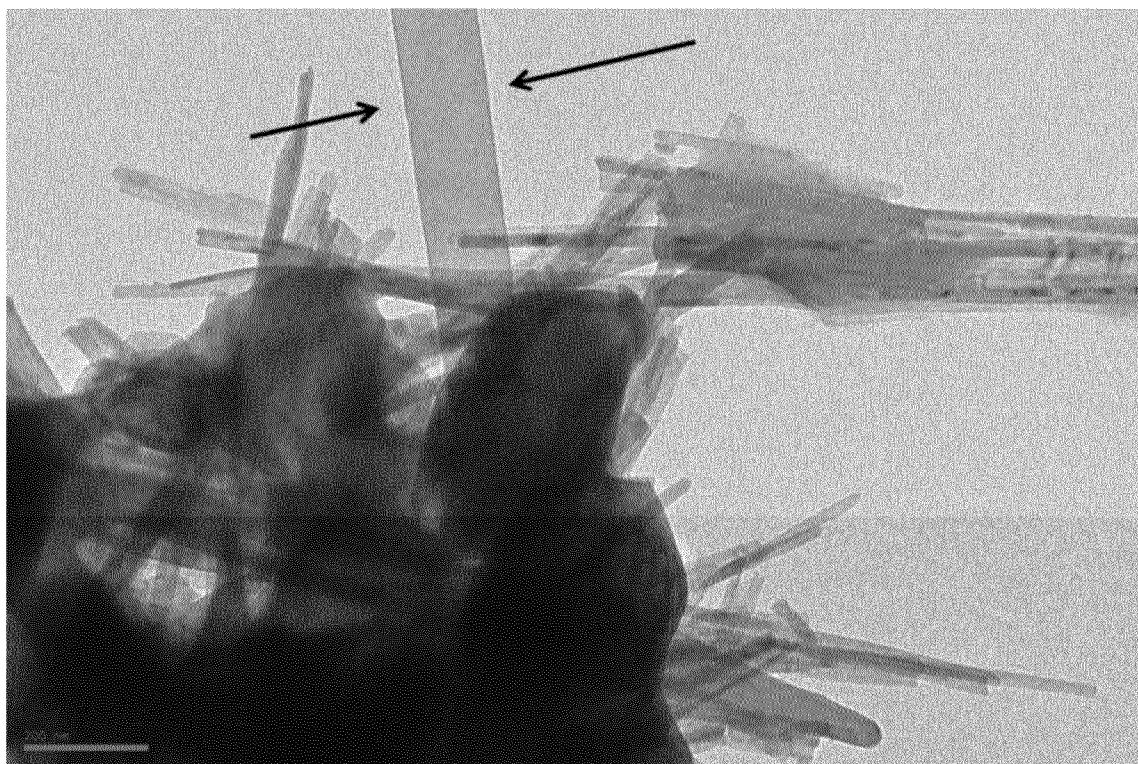


Fig. 17

Fig. 18

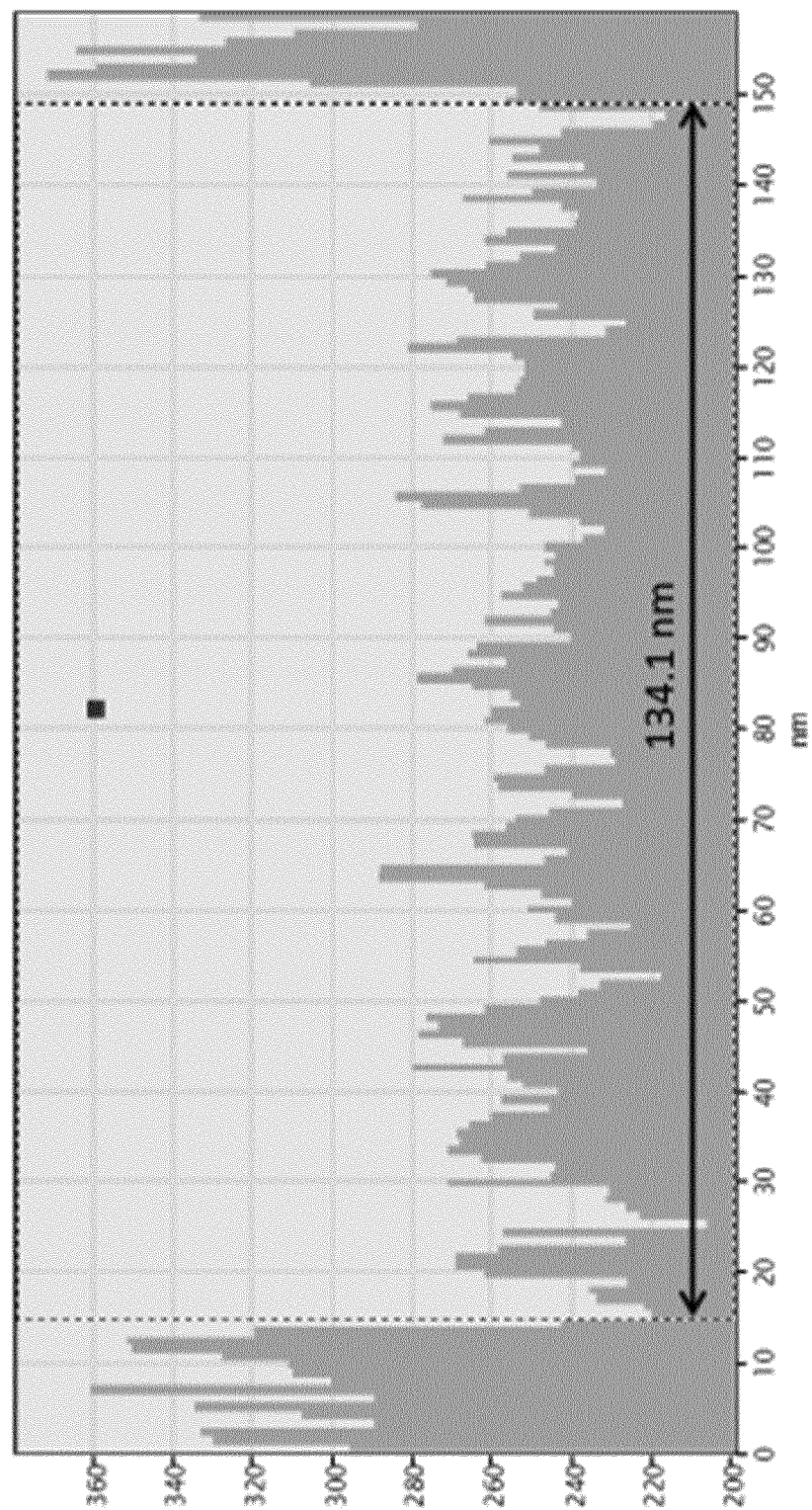
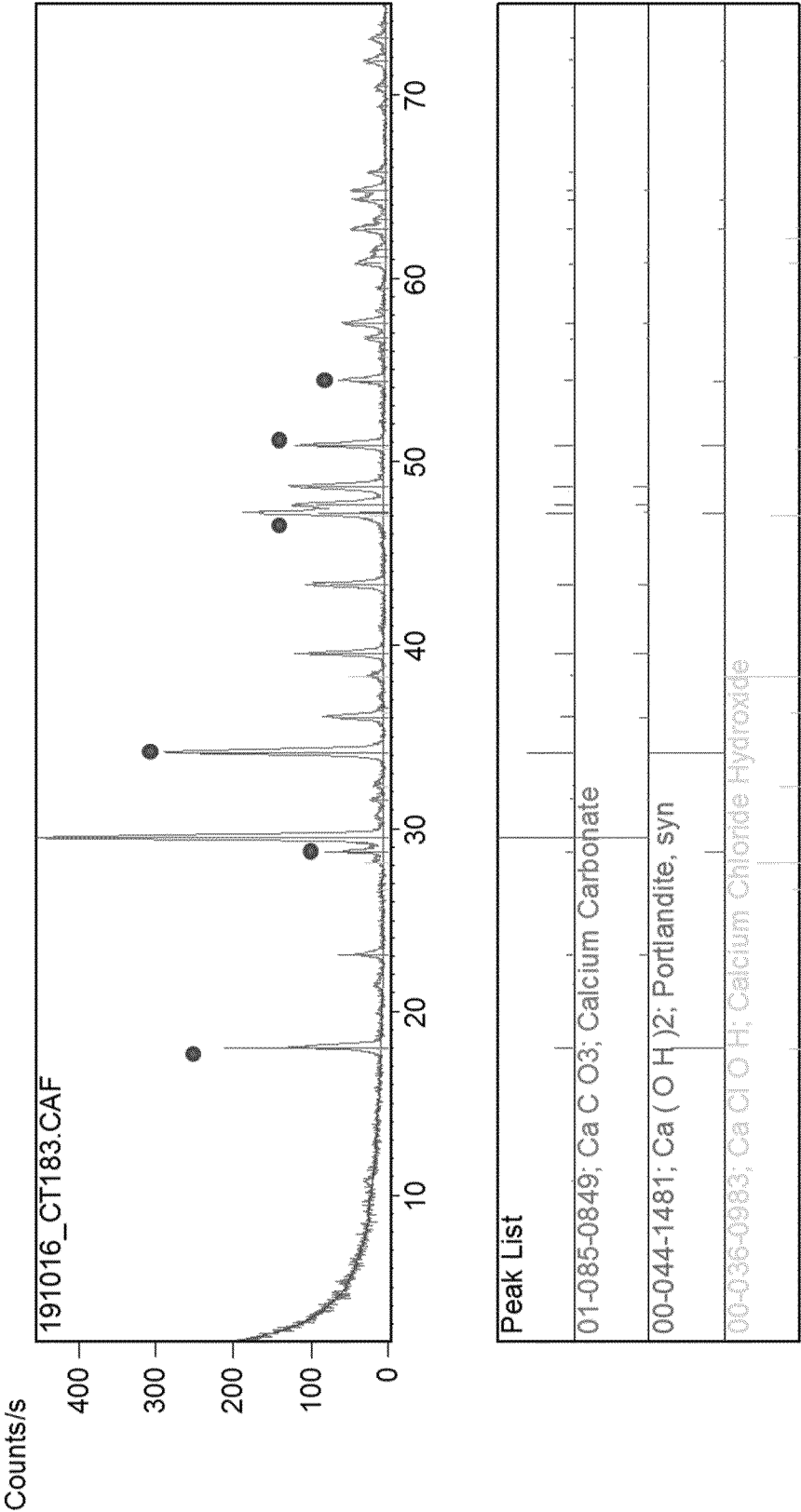


Fig. 19



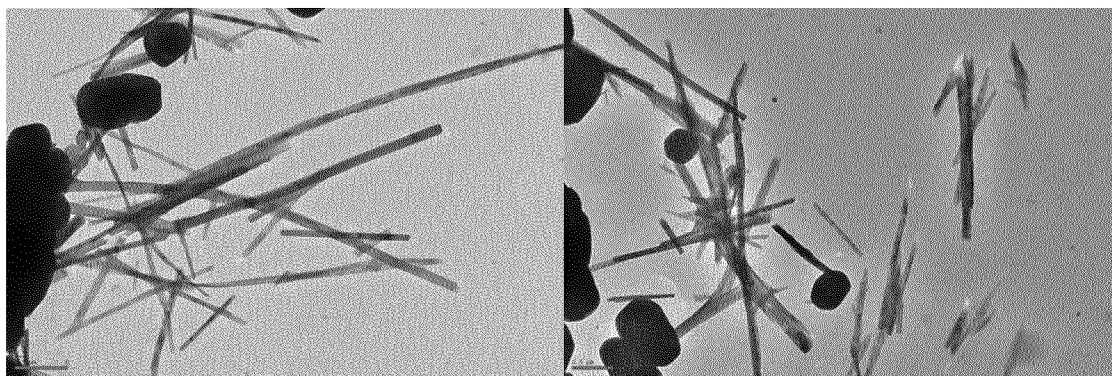


Fig. 20

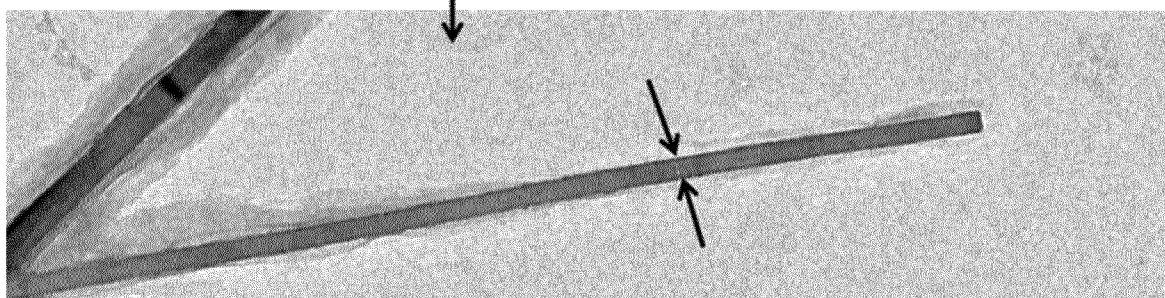
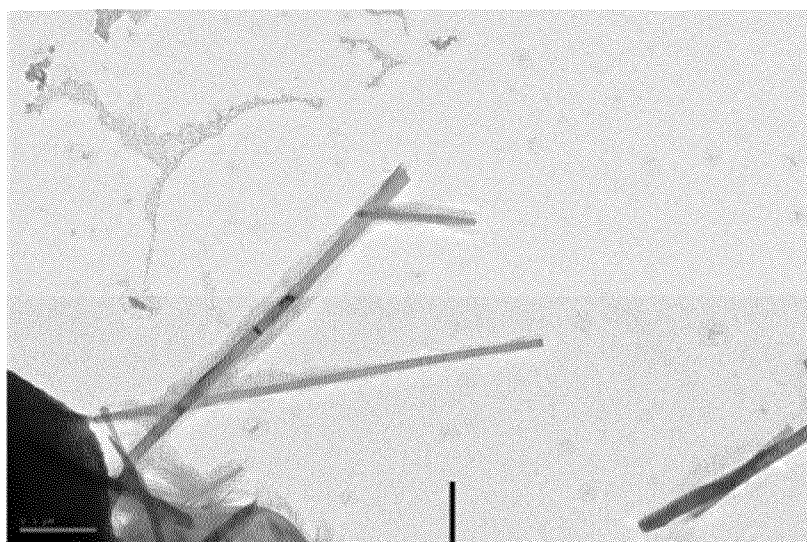
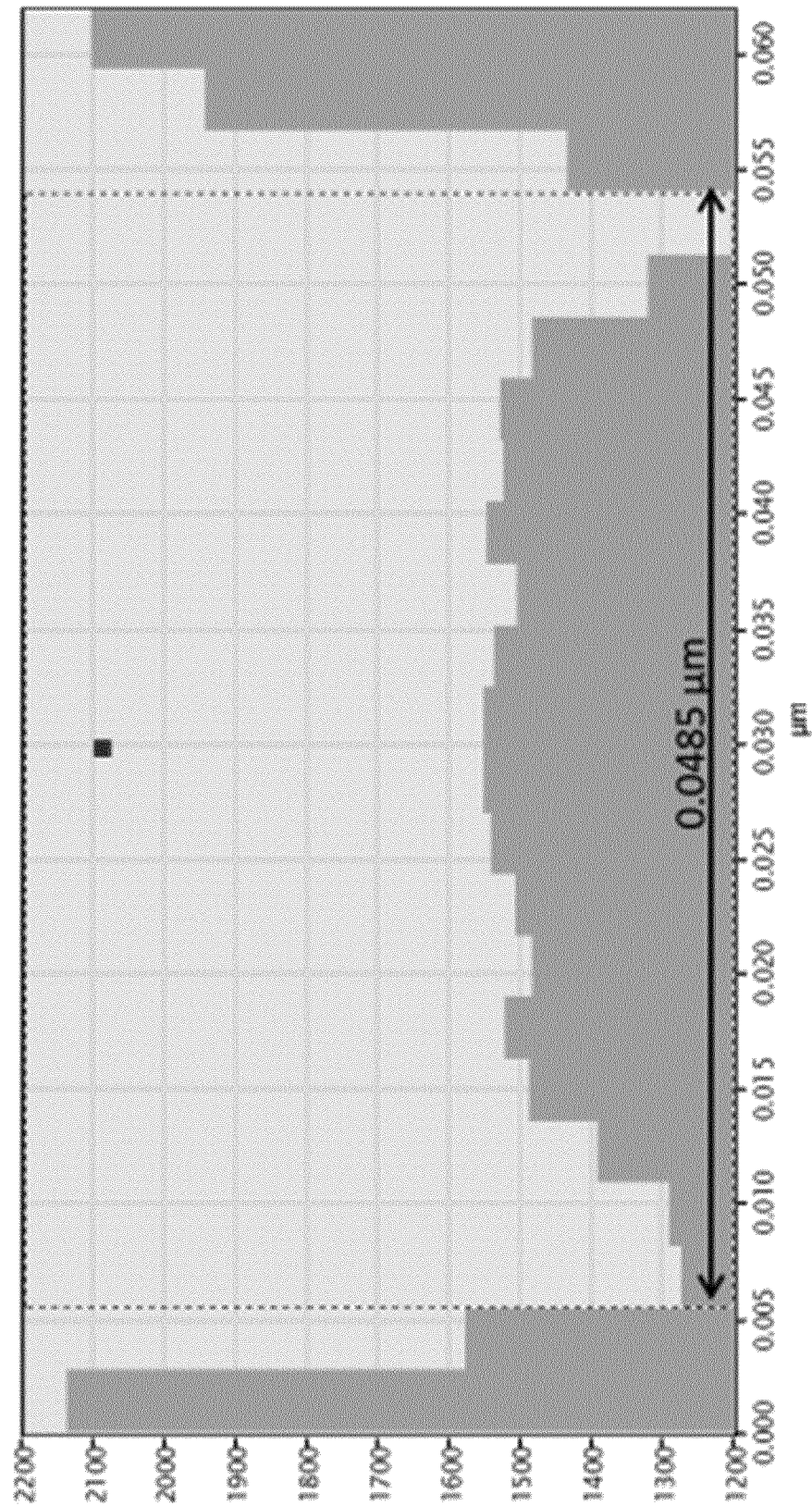


Fig. 21

Fig. 22



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/082839

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01F11/02 C04B2/06 C04B22/06 C04B20/00
ADD.

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)

C01F C04B

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)

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FARAH DIANA MOHD DAUD ET AL: "Fabrication of Ca(OH) ₂ Nanostructures by Facile Solution - Based Synthesis at Various Reaction Temperatures as CO ₂ Adsorbent", MATERIALS SCIENCE FORUM, vol. 756, 14 May 2013 (2013-05-14), pages 175-181, XP055285598, ISSN: 0250-9776, DOI: 10.4028/www.scientific.net/MSF.756.175 the whole document	1-13
A	US 7 892 447 B2 (MADDAN ORVILLE L [US]) 22 February 2011 (2011-02-22) claims 1, 17, 22	1-13



Further documents are listed in the continuation of Box C.



See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

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Date of the actual completion of the international search

8 June 2017

Date of mailing of the international search report

19/06/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
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Authorized officer

Stratford, Katja

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/082839

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WEILIU FAN ET AL: "Solvothermal synthesis of Mg(OH) ₂ nanotubes using Mg ₁₀ (OH) ₁₈ Cl ₂ . 5H ₂ O nanowires as precursors", JOURNAL OF MATERIALS CHEMISTRY, vol. 13, no. 12, 31 October 2003 (2003-10-31), pages 3062-3065, XP055285650, GB ISSN: 0959-9428, DOI: 10.1039/B307619A cited in the application the whole document	1-13
A	H. MANZANO ET AL: "Do Cement Nanotubes exist?", ADVANCED MATERIALS, vol. 24, no. 24, 26 June 2012 (2012-06-26), pages 3239-3245, XP055284911, DE ISSN: 0935-9648, DOI: 10.1002/adma.201103704 cited in the application the whole document	1-13
A	Hassouna Dhaouadi ET AL: "Mg(OH) ₂ Nanorods Synthesized by A Facile Hydrothermal Method in the Presence of CTAB Citation: Hassouna Dhaouadi, Hedia Chaabane and Fathi Touati, "Mg(OH) ₂ Nanorods Synthesized by A Facile Hydrothermal Method in the Presence of CTAB", 4 September 2011 (2011-09-04), pages 153-159, XP055284944, DOI: 10.3786/nml.v3i3.p153-159 Retrieved from the Internet: URL:http://www.nmletters.org/images/pdf/v4/v3n3/153-159(192).pdf [retrieved on 2016-07-04] cited in the application the whole document	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/082839

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