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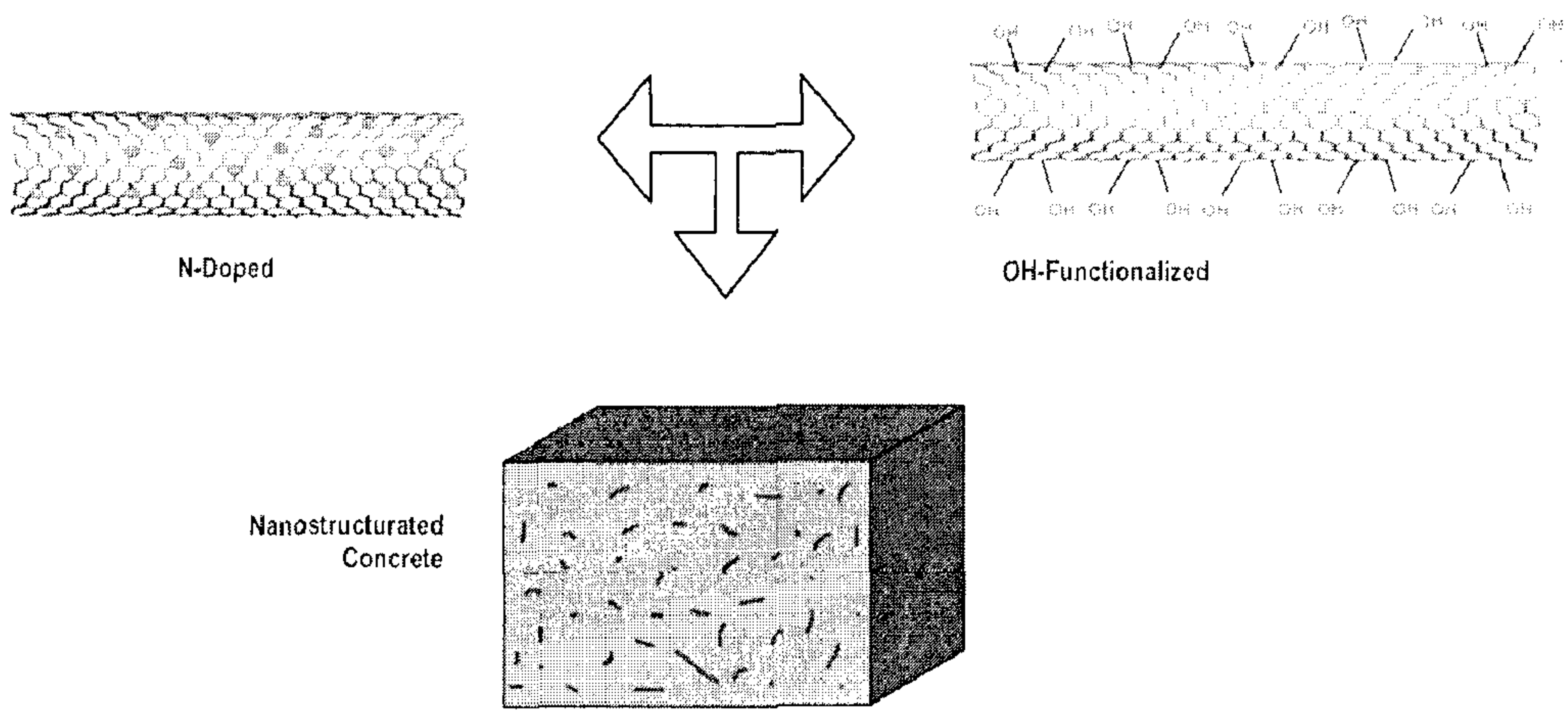
(54) **Titre :** BETON RENFORCE PAR DES NANOMATERIAUX HYBRIDES
(54) **Title:** CONCRETE REINFORCED WITH HYBRID NANOMATERIALS



(57) **Abrégé/Abstract:**
Concrete reinforced with nanostructures, comprising cement and a dispersion including water, a surfactant, carbon nanotubes having on the external surfaces thereof carbon atoms substituted by atoms of another element, and carbon nanotubes possessing chemical groups on the surface thereof.

ABSTRACT OF THE INVENTION

Concrete reinforced with nanostructures, comprising cement and dispersion including water, a surfactant, carbon nanotubes having on the external surfaces thereof carbon atoms substituted by atoms of other element, and carbon nanotubes possessing chemical groups on the surface thereof.

CONCRETE REINFORCED WITH HYBRID NANOMATERIALS

FIELD OF THE INVENTION

The instant invention is related to reinforced concretes, and particularly to concrete reinforced with nanostructured materials.

BACKGROUND OF THE INVENTION

In the construction industry there is a composite material generally used, a paste-type material comprising other materials to gain volume and that has excellent mechanical properties, this material is concrete. Through history, concrete has been suffering important modifications ranging from masonry binding to be a principal element in constructions of slim and resistant structures, such as reinforced concrete.

Concrete has different classifications primarily based on its ability to resist strains or strength under compression and the time required to acquire such strength (dry). In this manner, normal resistance concrete and high resistance or fast resistance concrete can be obtained. It is important to mention that there is a national and international industry that has generated diverse material to be combined with concrete in order it to acquire new properties. These materials are known as additives, fluidizers, die retardants, waterproofing agents, air fillers and strain-reinforce fibers. In other words, concrete is a mixture that can accept a number of external agents (additives) without detriment of its main feature (compressive strength) and with a gain in its original properties.

On the other hand, the interest in developing composite materials has been increased in recent years, combining two or more components and which properties allow their use in diverse areas. More recently, the interest in using nanometer-scale materials for manufacturing nanocompounds with improved properties has been increased. Carbon nanotubes are excellent candidates for manufacturing nanocompounds as these can be 100 times more strength than steel but six times lighter than this.

An example of the above is the document WO2009/099640 that discloses a method for manufacturing composite materials comprising cement rein forced with dispersed carbon nanotubes, by applying ultrasonic energy and using a surfactant to form a fluid dispersion of carbon nanotubes and mixing the dispersion with cement such that carbon nanotubes can be well dispersed in the cementitious matrix.

Also, document US2008/0134942 discloses the use of carbon nanotubes in cement composites, wherein cement, aggregated material, carbon nanotubes and plasticizer are used.

Within the different carbon nanotube types, there are single-wall structures and multiple-wall structures, besides a differentiation according to elements to be bound to nanotube walls by means of physical and/or chemical treatments. For example, carbon atoms can be replaced by different elements in the walls. Among these are nitrogen, phosphorus, potassium, silicon, oxygen, boron, etc. Additionally, there is possible that covalent groups to be covalently bound to nanotube walls, particularly methyl, carbonyl, hydroxyl groups, etc. The modification of tube surface either by doping or functionalizing, increases surface reactivity thereof, which is essential to create strong interactions among nanotubes and matrixes in question such as cement or concrete.

Considering that the nanostructures are able to transfer bulk properties to concrete matrix when mixing correctly, homogeneously and in adequate rate, and that hydraulic concrete of cement-water + aggregates may accept external agents, it is possible to generate a new family of nanostructured cements with improved mechanical properties by adding minimal amounts of nanomaterials (e.g. 0.1 - 10% by weight). In this regard, it is important to mention that the works of Matthew Brenner on the mixing of reinforced carbon nanofibers with carbon nanotubes (pures) in cement and concrete, wherein increments in compression strength of samples having these mixtures with respect to those lacking of additive are reported.

None of the above mentioned documents used doped or functionalized multiple-walls carbon nanotubes that importantly increase the load transference of tubes to concrete due to the doping or functionalized sites of nanotubes.

In general, concrete can be considered as a series of spore bound giving the compound a high strength since they are "urchin"-like inter-bound, such structure handles better the strength as the urchins are not inter-bound by their points and they separate under stress, the present invention is related to the integration of such crystalline structures catalyzing the same in the wall of our tubes. Upon doping such nanotubes they become more reactive allowing such a binding, binding so the spores with a similar size element such as the nanotube, obtaining in this manner a double effect, upon compression the tubes binding spore to spore act as a containment, increasing their compressive strength, and upon stress the tube acts as a tensor between spores growing in its surface.

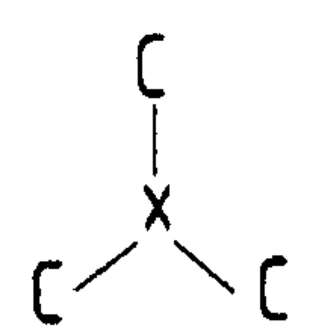
By hybrid materials according to the present invention, is meant the inclusion of doped nanotubes (bamboo type), nanobars of SiOx and nanoplates (or nanoflakes of SiOx, AlOx).

It is important to mention that the use of doped nanotubes and particularly nitrogen-doped nanotubes, when mixing with concretes, they promote the growth of nanostructures of SiOx (flakes and bars) increasing by two the concrete mechanical properties. When nitrogen-doped nanotubes are not added but other nanotubes (such as those of the above cited documents, wherein non nitrogen-doped materials are used) are added, these new structures of SiOx and AlOx NO interact with nanotubes. Therefore, the combination of nitrogen-doped nanotubes, SiOx and AlOx flakes and SiOx nanobars form a new hybrid nanomaterial which is more resistant within the concrete.

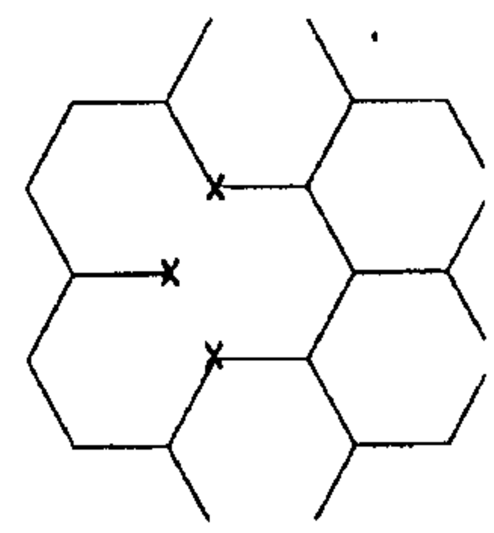
In the state of art the tubes have perfect crystalline nets but the inventive doping generates imperfections in the tubes, therefore the graphitic net is not perfect.

Firstly: the term "doped tubes" is applicable to a substitution of elements in the arrangement of a non- perfect graphitic net, wherein three types of doping are:

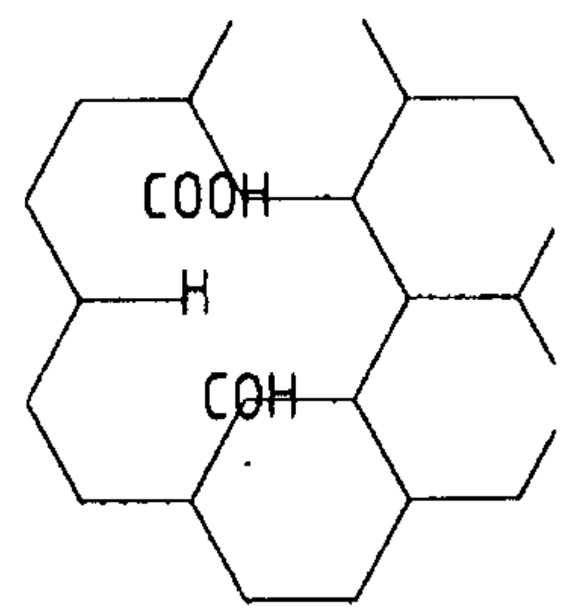
Type I: carbon atom substitution (with any atom available) in the graphitic net with no vacancy.



Type II: carbon atom substitution (with any atom available) in the graphitic net with vacancy.



Type III: carbon atom substitutions (with hydrogen -H, or carbonyl or carboxyl groups -COH or COOH) with sites having general vacancy.



In all cases, x is ranging from 0.1 to 10% at (atomic percent), x=H, N, P, OX, S, Si, Se, B ………carbonyl, carboxyl groups including any combination or permutations.

Second: In addition to the doping, the tube dimensions and also the aspect ratio are different with respect to the previous referred works.

Third: in the described nanostructured concrete of the invention, combinations of nanomaterials are given but reinforce mechanism are different:

1. with multiple wall or multilayer nanotubes (MWNT'S), with an imperfect graphitic net, having diminished Type III doping (<2-3% at), and a lower reactivity

with oxygen. No different nano-structures are present compared to those added (that is, the nanotubes), the moderated increment in strength is due to the nanotubes and their distribution within material.

2. with COx, having an imperfect net with Type III doping (3-5% at) and a moderated reactivity with oxygen. Neither nanostructures of SiOx or AlOx are present upon adding nanotubes, the moderated increment in strength is due to the presence of nanotubes and its distribution in the material.
3. with CNx, having an imperfect net with Type I and II doping (0.1-10% at), with high reactivity to oxygen. An hybrid nanostructures arrangement consisting in nanofibers and nanoplates of SiOx and AlOx is present, with the presence of CNx. Due to its high reactivity, the SiOx and AlOx structures are catalyzed by tubes of CNx, and the result is not only a mixture of nanotubes and cement with water, but CNx nanotubes are catalyzed during the mixing of cement and water by means of an exothermic reaction forming nanofibers and nanoplates of SiOx and AlOx, creating a modification in nanometric structure of concrete that has not been previously reported.

Fourth: The carbon nanotubes that perform better are those N-doped, and their structure is bamboo-type and this is not disclosed in any of the prior art patents and, in fact, they are not exactly tubes themselves based in their physical structure.

The applications of a concrete manufactured according to the present invention are so wide as the use of the concrete itself in these days, the construction industry is not limited to a particular sector, but it embodies from the greatest civil constructions such as dams, power stations, communication paths, and complex buildings with great size and volume, and also the housing sector wherein applicability of this material is of great importance because of the following reasons.

- As the inventive concrete is more strength than the usual concrete, less amount of concrete is required for the construction of hosing structural elements, and therefore more habitable area is available.
- As the structural elements involved have less thickness, the related weight of such elements is also less, therefore the handling of the same is simplified and less personnel or labor is required for handling thereof.
- As the structural elements are lighter and more easily to handle, their manufacturing is simplified in controlled environments for pre-manufacturing a structure, allowing the industrialization of concrete

pre-manufactured houses.

- By diminishing the amount of cement used, the ecology is preserved as a ton of cement produced is equivalent to a ton of CO_2 produced.
- Decorative elements of any type of facades will require less thickness to support pressures caused by winds and their usual strength demands, and therefore it means a lower weight of the main structure saving in this manner the basement costs of structure.

SUMMARY OF THE INVENTION

Therefore, an object of the invention is to provide a reinforced concrete, characterized by comprising cement and a dispersion including water, a surfactant, multilayer carbon nanotubes wherein carbon atoms in their external walls are substituted by atoms of other element and multilayer carbon nanotubes having chemical groups in their surface.

In addition, another object of the invention is to provide a method for reinforcing concrete, comprising the steps of forming a surfactant dispersion, multilayer carbon nanotubes having carbon atoms in their external walls substituted by atoms of other element and multilayer carbon nanotubes having on their surface chemical groups; and mixing the dispersion with cement to form reinforced concrete.

BRIEF DESCRIPTION OF THE FIGURES

For a better understanding of the invention, a disclosure thereof is provided below along with drawings accompanying the same, wherein:

Figure 1a shows carbon nanotube models with different orientations of the hexagons;

Figure 1b is a scheme of a graphene sheet and a nanotube with single-wall zigzag structure;

Figure 2 is a diagram of the synthesis process for the synthesis of carbon nanotubes, using chemical vapor deposition assisted by spraying (AACVD), and of the packed growing of nanotubes.

Figure 3a is an X-ray diffraction pattern of nanotubes;

Figure 3b is an image showing crystallinity of nanotubes;

Figure 3c is a high resolution transmission electron microscope image of nanotubes;

Figure 4 is a graphic performed by electronic scanning for Portland cement;

Figure 5a, 5b and 5c are scanning electron microscope micrographs illustrating morphology of grey or Portland cement, as well as the particle size, ranging from 1 µm to 15 µm;

Figure 6 is a scheme showing the addition concept of two types of nanotubes to cement to obtain the new nanostructured compound material;

Figures 7a and 7b are micrographs obtained by a scanning electron microscope, wherein the aligned packed of doped carbon nanotubes with functional OH groups are shown;

Figure 8a a is a scheme of simultaneous ultrasonic dispersion process;

Figure 8b is a scheme of the effect the surfactant agent causes on the carbon nanotube packages and the aqueous media, which is translated in an homogeneous dispersion, further compatible for manufacturing the subject concrete mixture;

Figure 9a is a scheme of the PVC mold used for manufacturing reinforced concrete test tubes;

Figure 9b illustrates a reinforced concrete test tube used in mechanical strength tests:

Figures 10a, 10b and 10c show micrographs of dispersion with nanotubes in different percentages, in the lower part of each figure there is a image in great detail of the same sample; and

Figures 11a, 11b, 11c and 11d show nanotube blocks dispersed and catalyzed nanometric structures.

DETAILED DESCRIPTION OF THE INVENTION

The agents used to reinforce concrete, are carbon nanostructures known as nanotubes, that are cylinder structures of multiple concentric layers disposed by tube-form graphene walls or nets (carbon hexagonal nets)(Fig. 1). The carbon atoms within these graphene cylinders are strongly linked by covalent bindings. It is to be noticed that the carbon-carbon binding is one of the most resistant or strength existing in nature. However, some of the carbon atoms in the hexagonal nets can be replaced by other elements or functional groups becoming these tubes more reactive and that their interactions with different matrixes being greater. Within the groups or elements that can replace carbon atoms can be listed N. P, O, S, Si, B, Se, etc, or any functional group -OH, -OOH, or OH.

The dimensions of multiple layer carbon nanotubes used in this invention have a mean length of 300 µm and diameters of 30-70 nm, an were synthesized by the AACVD method (Aerosol Assisted Chemical Vapor Deposition), which uses a solution containing carbon source and a catalyst responsible for the growing (e.g. transition metals such as Ni, Fe and Co). This solution is ultrasonic processed in order to generate an aerosol (Fig. 2) and by means of an inert gas it is transported through a quartz tube to high temperature reactors wherein the growing of nanotubes occurs.

Other important features of nanotubes of the instant invention are:

- Reactivity, caused by doping or functional groups, which allows a geater interaction between carbon nanotube and the matrix in question to manufacture the nanocompound.
- Excellent crystallinity degree of nanotubes (Fig.

3b).

- Excellent purity of nanotubes that can be observed in figures 3a, 3b and 3c.

The Portland cement used in this invention is formed by the following oxides according to the list shown below:

64% calcium oxide,

21% silicon oxide,

5,5% aluminium oxide,

4,5% iron oxide

2,4% magnesium oxide

1,6% sulfates

1% other materials, mainly water.

In order to characterize Portland cement used in our experiments, a previous trial of the particle size using scanning electron microscope (Fig. 4), as well as an analysis of the material chemical composition, using X-ray energetic dispersion technique (EDX) were carried out. In figures 5a-5c micrographs of scanning electron microscope are shown, illustrating morphology of grey or Portland cement in different resolutions as well as particle size from 1 µm to 15µm.

Element	% by weight	% AT
Ca	39.45	22.21
O	35.43	49.96
C	8.3	15.59
Si	6.47	5.2
S	4.19	2.95
Al	2.07	1.73
Fe	1.97	0.8
K	1.15	0.66
Mg	0.97	0.9

The aim of this invention is the study of utilization of mechanical properties of doped and functionalized carbon nanotubes and in order to increase mechanical properties of concrete using minimal amount of nanotubes. The key of this invention is related to the interaction of active sites on the nanostructure surface (doping), that is, using carbon nanotubes with doped external walls (carbon atom substituted by atoms of other elements; Fig. 6) as well as that having surface functional groups (functionalized with chemical groups with those above mentioned; Fig. 6), taking advantage of aspect ratio (length/diameter) of carbon nanotubes, aspect ratio unique with regard to other materials used as aggregated before; the nanotube aspect ratios used ranging from 30,000 to 50,000.

Nanotube Dispersion in a suitable medium

In concretes, the concrete-water mixture defines its mechanical strength. Therefore, it is possible to perform the mixing of nanotubes in two ways: a) dispersing them in cement, or b) dispersing them in water and afterwards in cement. Since dispersions in cement are less feasible due to the consistency of material when manufacturing, the most convenient is to carry out homogenous dispersions of nanotubes in water that will be added later to cement.

Initially the nanotubes are disposed in aligned arrangements such as bundles and these arrangements in general are hydrophobic, making difficult a homogeneous dispersion in the medium. Due to this reason, it is important to use a surface active agent or surfactant in order to carry out homogeneous dispersions of nanotubes, thus obtaining the suitable medium for the preparation of reinforced concrete with carbon nanotubes. In Figures 7a and 7b there is shown the aligned packing of carbon nanotubes doped with functional groups and doped with nitrogen respectively.

For preparing dispersions in cases of doped and/or functionalized multiple-wall carbon nanotubes, different rates based on the weigh percentage of nanotubes with respect to cement weight to be used for manufacturing the mixture in question were used. In particular, an Erlenmeyer flask containing a usual surfactant (liquid detergent with pH 9, also it is possible using SDS or other type of surfactant) in water at 0.3% with respect to water volume (Fig. 8). Afterwards, a process of dispersion was used, by immersing the flask in an ultrasonic bath (using an electroacustic transducer of 42 kHz in a 30-minute continuous cycle) and simultaneously disposing within the flask an ultrasonic point of 500 watts with sonication pulses of 5 minutes and 3 minutes of stop. In Figure 8b, the effect caused by the surfactant on the carbon nanotubes is shown (left side) and the aqueous media, which results in a homogeneous dispersion (right side), further compatible for performing the concrete mixture.

Manufacturing of control test tubes

The experimental design for obtaining nanostructured reinforced concrete, using doped or functionalized carbon nanotubes, comprises the manufacturing of test tubes having dimensions according to ASTM norms (American Society Testing of Materials). Different samples with different doped or functionalized nanotubes concentrations were obtained. For instance, the following weight percentages were used that are indicated with respect to weight of grey or Portland cement: 1.0%, 0.1% and 0.01%.

The mold is obtained from a PVC tube cut in segments of

10 cm in length, in which a cross-cut is effected in order to make easy the extraction of the test tube once the concrete dried and became solid state (Figures 9a and 9b).

The experimental result were given statistically by using two test tubes with a mixture of 400 g with grey Portland cement, 200 ml of aqueous solution with 0.3% of surfactant (pH 9).

For mixing doped and functionalized carbon nanotubes, 200 g of grey cement were poured in a plastic container, afterwards, the aqueous solution is poured slowly (said solution carrying the dispersed carbon nanotubes) mixing manually continuously. Finally, the alkalinity degree is measured, obtaining thus a pH of approximately 12.

Afterwards, molds are placed on a wood plate covered with a plastic film in order to avoid the loss of moisture due to the base solution, and the mixture of cement-nanotubes is poured therein. Upon completing the pouring, a plastic film is placed on the mold top (in order to avoid the excessive loss of moisture).

After 24 hours, the test tubes are extracted from molds such that the test tubes are slipped downwards. The test tube is placed into a plastic container in a brace a little higher than the test tube to be cured for 24 hours.

After the curing time has finished, the test tubes are withdrawn from the liquid media and are placed on a surface, with a moist cloth and superficially dry, the test tubes are cleaned to delete the water in excess from its surface and are tagged according to the type of mixture.

A set of four test tubes is fixed for each mixture type having 1 control and 3 test samples. The difference in the series of mixtures is the type of aqueous solution added to cement. Said solution is differenced according to the doped nanotube type that carries, according also to the nanostructure concentration that carries that ranges from 0.01% to 1.0% by weight of cement.

It is important to mention that during preparation of aqueous solutions with carbon nanotubes, it was observed that for percentages from 0.01% to 0.1% by weight, the dispersions are very homogeneous and practically no nanotube conglomerates are observed (Fig. 10a and 10b), contrary to the rest of concentrations wherein lumps and conglomerated appeared. For percentages of 1% by weight of doped or functionalized nanotubes, the aqueous solution was highly saturated: 4 g of carbon nanotubes in 200 ml of water plus 0.3% of surfactant (Fig. 10c). The phenomenon of extreme viscosity is observed after about 5 minutes from initiation of the dispersion process and therefore the solution is increasingly becoming more viscous, thus reducing the cavitation effectiveness, which results in some sites with carbon nanotube packages, especially when carbon nanotubes are nitrogen-doped.

The test tubes were compressed to rupture by simple compression using a 120 ton capacity hydraulic press, all test tubes were deposited on and covered with neoprene-coated steel plates (press accessories) to standardizing the strength applied to the cross-section of cylinder, resulting in each case in a associated compression to each test tube.

Mixture	Description
2	White cement + Water without forging
3	Grey cement + (Water, additive)[4,1]
4	White cement + (Water, additive) [4,1]
5	Grey cement + (Water, 0.3% Surfactant)
6	Grey cement + (Water, 0.3% Surfactant) + [0.01%wt]MWCNT_NX
7	Grey cement + (Water, 0.3% Surfactant) + [0.1%wt]MWCNT_NX
8	Grey cement + (Water, 0.3% Surfactant) + [0.01%wt]MWCNT_OX
9	Grey cement + (Water, 0.3% Surfactant) + [0.1%wt]MWCNT_OX
11	Grey cement + (Water, 0.3% Surfactant) + [1.0%wt]MWCNT_NX
12	Grey cement + (Water, 0.3% Surfactant) + [1.0%wt]MWCNT_OX
13	White cement + {(Resin, Additive)[2,1]} + (0.1%wt_resin)MWCNT_OX
14	Grey cement +Water+ ({(Resin, Additive)[2,1]} + (0.1%wt_resin)MWCNT_OX)
17	Grey cement +Water+ {(Resin, Additive)[2,1]}3,1

Mixture	#	D [cm]	H [cm]	A [cm2]	V [cm3]	P [g]	ρ [g/cm3]	Pu [kg]	σ [kg/cm2]	σ [MPa]
2	1	3.8	9.2	11.34	104.34	179	1.72	900	76.36	7.78
	2	3.9	9.5	11.95	113.49	179	1.58	1800	150.68	14.78
	3	3.9	9.5	11.95	113.49	185	1.63	1200	100.45	9.85
	4	3.9	9	11.95	107.51	167	1.55	1200	100.45	9.85
3	1	3.8	9.6	11.34	108.88	184	1.69	2200	193.98	19.03
	2	3.8	9.6	11.34	108.88	181	1.66	4400	387.97	38.06
4	1	3.8	8.5	11.34	96.40	144	1.49	3000	264.52	25.95
	2	3.8	9.6	11.34	108.88	155	1.42	2200	193.98	19.03
	3	3.8	9.7	11.34	110.01	159	1.45	2000	176.35	17.30
5	1	3.9	9.5	11.95	113.49	181	1.59	2000	167.42	16.42
	2	3.9	9.5	11.95	113.49	174	1.53	1800	150.68	14.78
6	1	3.8	9.6	11.34	108.88	184	1.69	3800	335.06	32.87
	2	3.8	9.6	11.34	108.88	184	1.69	2200	193.98	19.03
7	1	3.8	9.4	11.34	106.61	173	1.62	3000	264.52	25.95
	2	3.8	9.4	11.34	106.61	175	1.64	3800	335.06	32.87
	3	3.8	9	11.34	102.07	166	1.63	2200	193.98	19.03
8	1	3.9	8.4	11.95	100.35	154	1.53	2400	200.91	19.71
	2	3.9	9.3	11.95	111.10	174	1.57	3200	267.87	26.28
	3	3.9	9.4	11.95	112.29	173	1.54	3400	284.62	27.92
9	1	3.9	8.8	11.95	105.12	164	1.56	1400	117.19	11.50
	2	3.9	9	11.95	107.51	162	1.51	1000	83.71	8.21
	3	3.9	8.8	11.95	105.12	155	1.47	1800	150.68	14.78
11	1	3.9	9.3	11.95	110.10	158	1.42	1400	117.19	11.50
	2	3.8	8.9	11.34	100.94	147	146	2800	246.89	24.22
	3	3.8	8.9	11.34	100.94	148	1.47	1200	105.81	10.38
12	1	3.8	8.8	11.34	99.80	144	1.44	1100	96.99	9.51
	2	3.8	8.9	11.34	100.94	144	1.43	1000	88.17	8.65
	3	8.9	8.6	11.95	102.73	144	1.40	900	75.34	7.39
13	1	3.8	9.4	11.34	106.61	181	1.70	4000	352.70	34.60
	2	3.8	9.7	11.34	110.01	190	1.73	1800	158.71	15.57
14	1	3.8	9.7	11.34	110.01	158	1.44	1100	96.99	9.51
	2	3.9	9.3	11.95	111.10	153	1.38	1000	83.71	8.21
17	1	4	10	12.57	125.66	194	1.54	900	71.62	7.03
	2	3.9	9.5	11.95	113.49	183	1.61	900	75.34	7.39

Once the reinforced concrete test tubes have been subjected to mechanical tests to analyze the compressive strength, important results were obtained. Significant increments in mechanical properties for reinforced test tubes were observed, with percentages of 0.01% of nitrogen-doped carbon nanotubes, as well as, the dispersion of nanostructures in the concrete matrix was observed (Figures 11a-11d).

In images shown in Figures 11a-11d there can be seen nanotube blocks that were not totally dispersed in some cases, and also crystalline forms that can be a reaction product between cement and water and the doped carbon nanotubes. The form in which nanotubes catalyze on their active surface the crystalline structures, allows us to deduct a suitable behavior pattern between the two structures, phenomena that probably cause the improvement of mechanical properties of concrete.

The present invention has been disclosed in its preferred embodiment, however, it is evident for those skilled in the art, that multiple changes and modifications on this invention can be made without go beyond the scope of the following claims.

CLAIMS

1. A reinforced concrete, characterized by comprising:

a cement and a dispersion including water, a surfactant, multilayer carbon nanotubes wherein the carbon atoms in their external walls are substituted by atoms of other elements and multilayer carbon nanotubes including chemical groups on their surface;

wherein the concentration of multilayer carbon nanotubes is 0.01% to 0.1% by weight of cement.

2. The reinforced concrete according to claim 1, characterized in that the cement is Portland cement.

3. The reinforced concrete according to claim 1, characterized in that the other element is selected from the group consisting of nitrogen, hydrogen, phosphorus, oxygen, sulfur, silicon, selenium and boron.

4. The reinforced concrete according to any of claims 1 or 3, characterized in that the chemical groups are selected from the group consisting of carbonyl group and carboxyl group.

5. The reinforced concrete according to claim 1, characterized in that the carbon nanotubes are doped nanotubes.

6. A method for reinforcing concrete, comprising the steps of:

forming a dispersion of surfactant, multilayer carbon nanotubes wherein carbon atoms on their external walls are substituted by atoms of other elements and multilayer carbon nanotubes having chemical groups on their surface; and

mixing the dispersion with cement to form a reinforced concrete;

wherein the concentration of multilayer carbon nanotubes is 0.01% to 0.1% by weight of cement.

7. The method for reinforcing concrete according to claim 6, characterized in that cement is Portland cement.

8. The method for reinforcing concrete according to claim 6, characterized in that the other element is selected from the group consisting of nitrogen, hydrogen, phosphorus, oxygen, sulfur, silicon, selenium and boron.

9. The method for reinforcing concrete, according to claim 6, characterized in that chemical groups are selected from the group consisting of carbonyl group and carboxyl group.

10. The method for reinforcing concrete according to claim 6, characterized in that the dispersion is carried out by sonication.

11. The method for reinforcing concrete according to claim 6, characterized in that the carbon nanotubes are

multiple wall carbon nanotubes.

12. The method for reinforcing concrete according to claim 6, characterized in that carbon nanotubes are doped nanotubes.

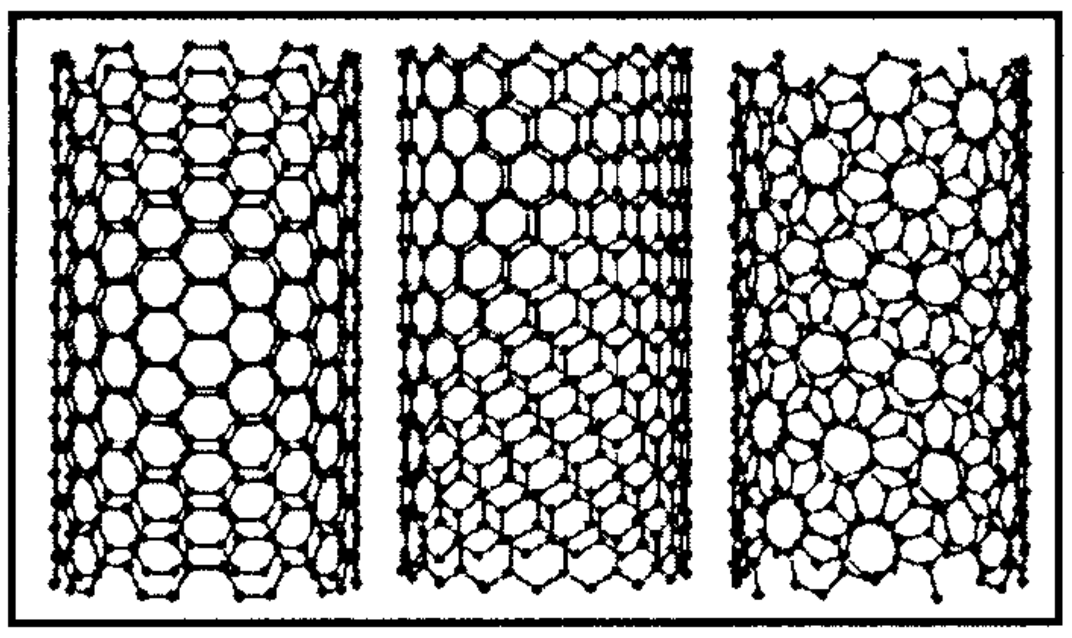


Fig.1a

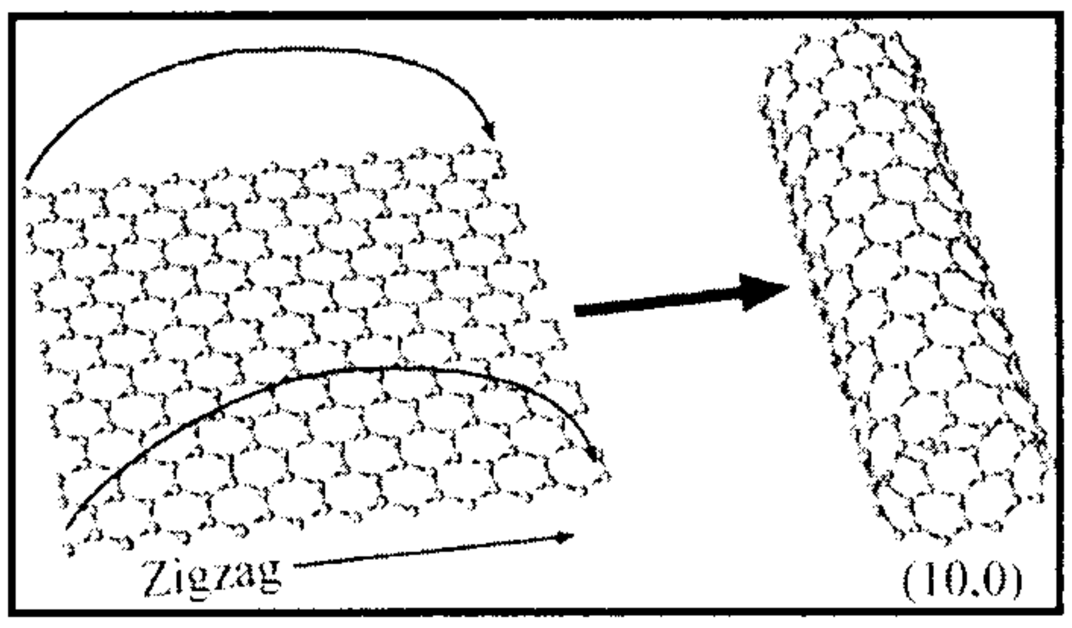


Fig. 1b

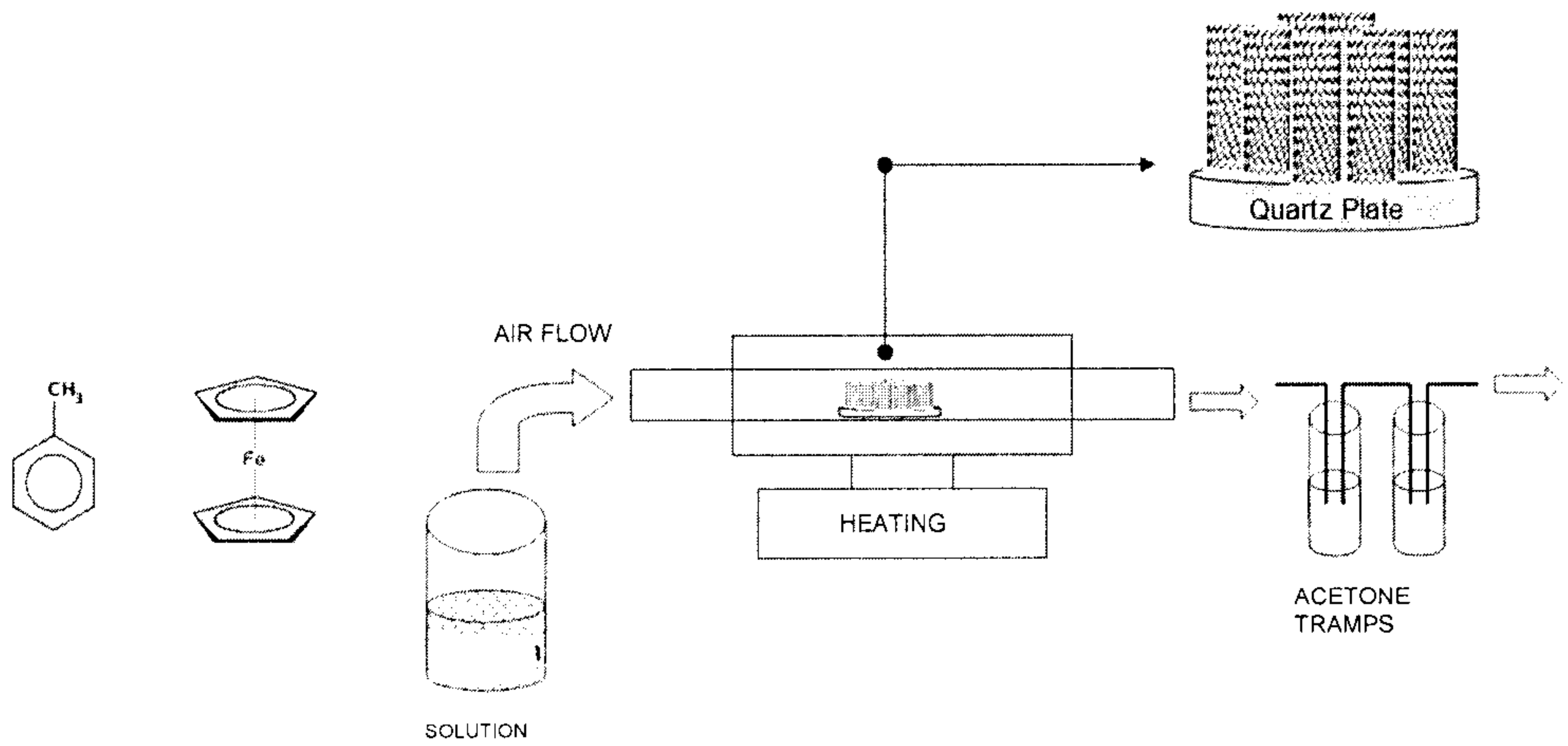
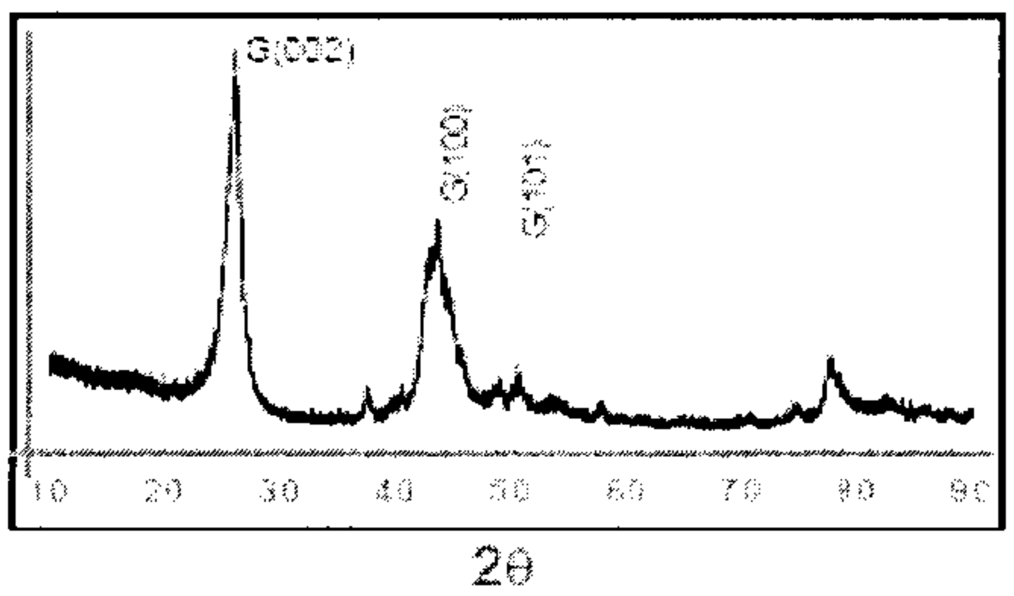


Fig. 2



X RAY diffraction Pattern

Fig. 3a

Fig. 3b

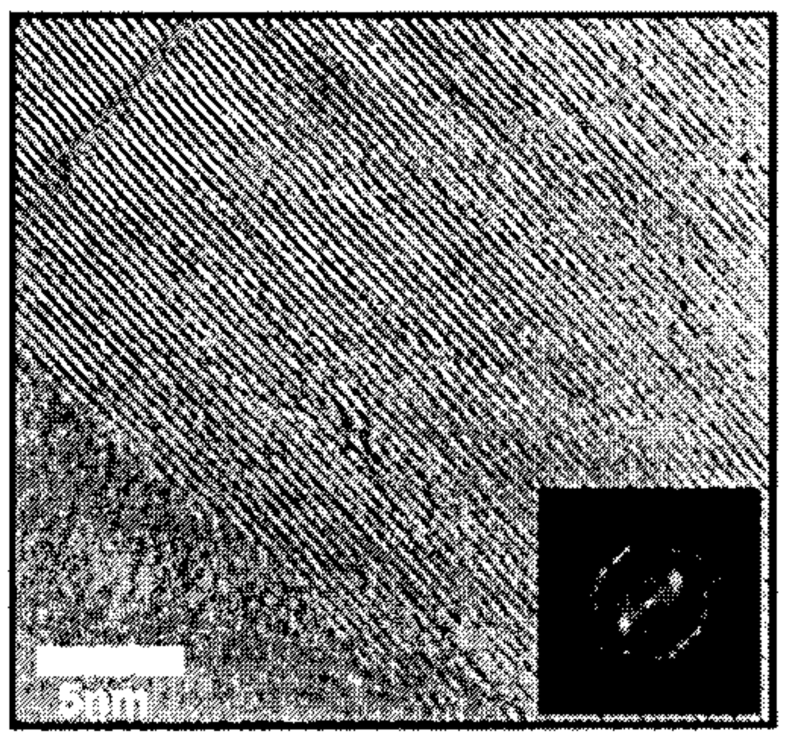


Fig. 3c

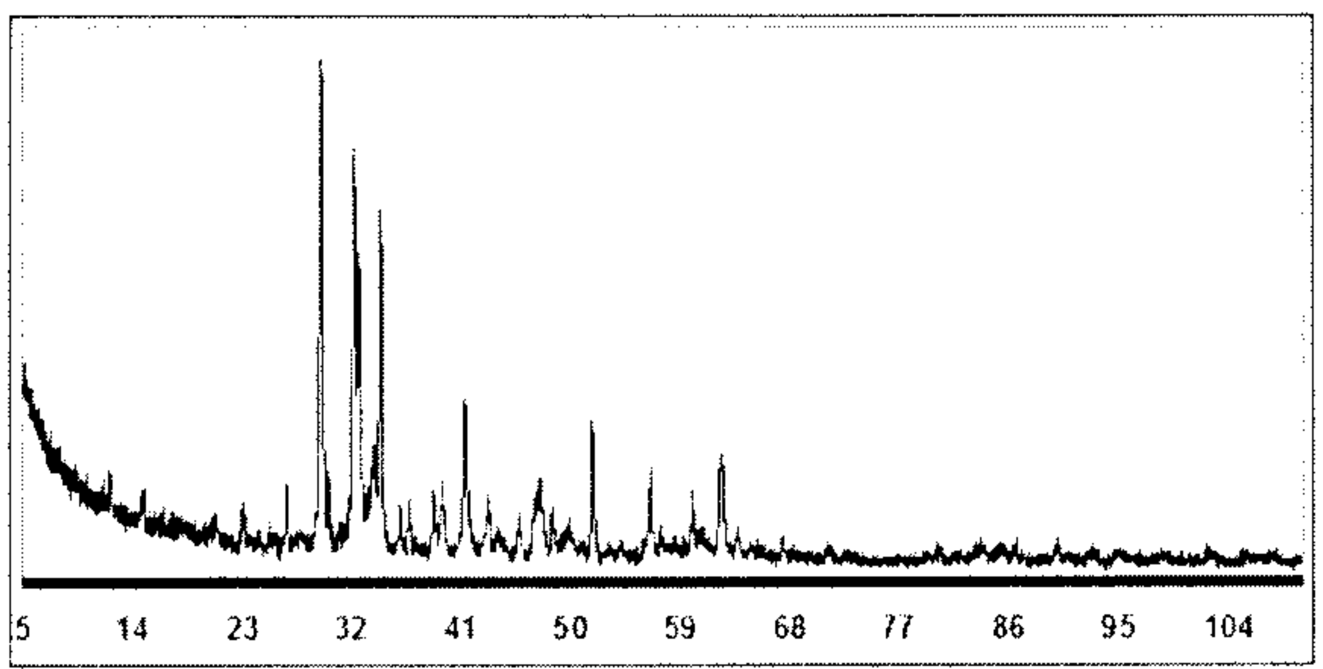


Fig. 4

Fig. 5a

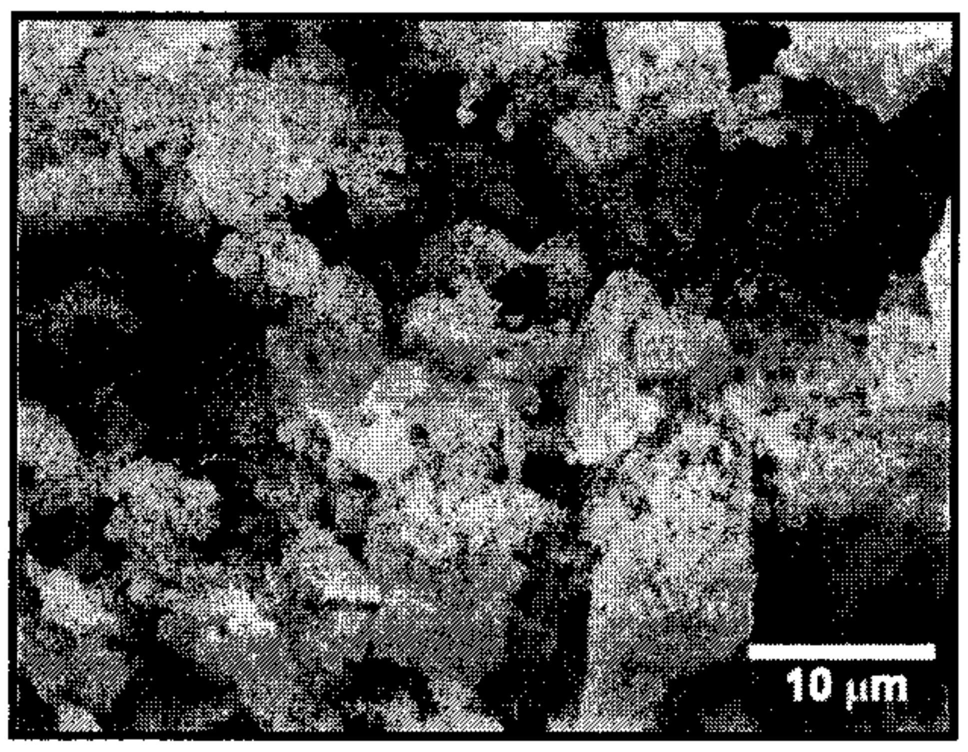


Fig. 5b

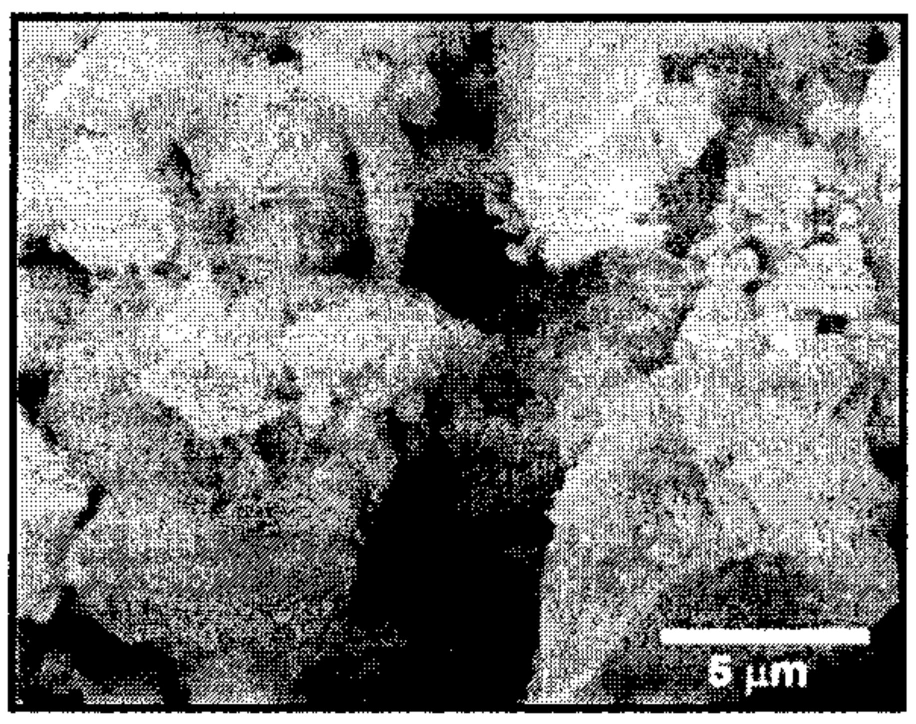


Fig. 5c

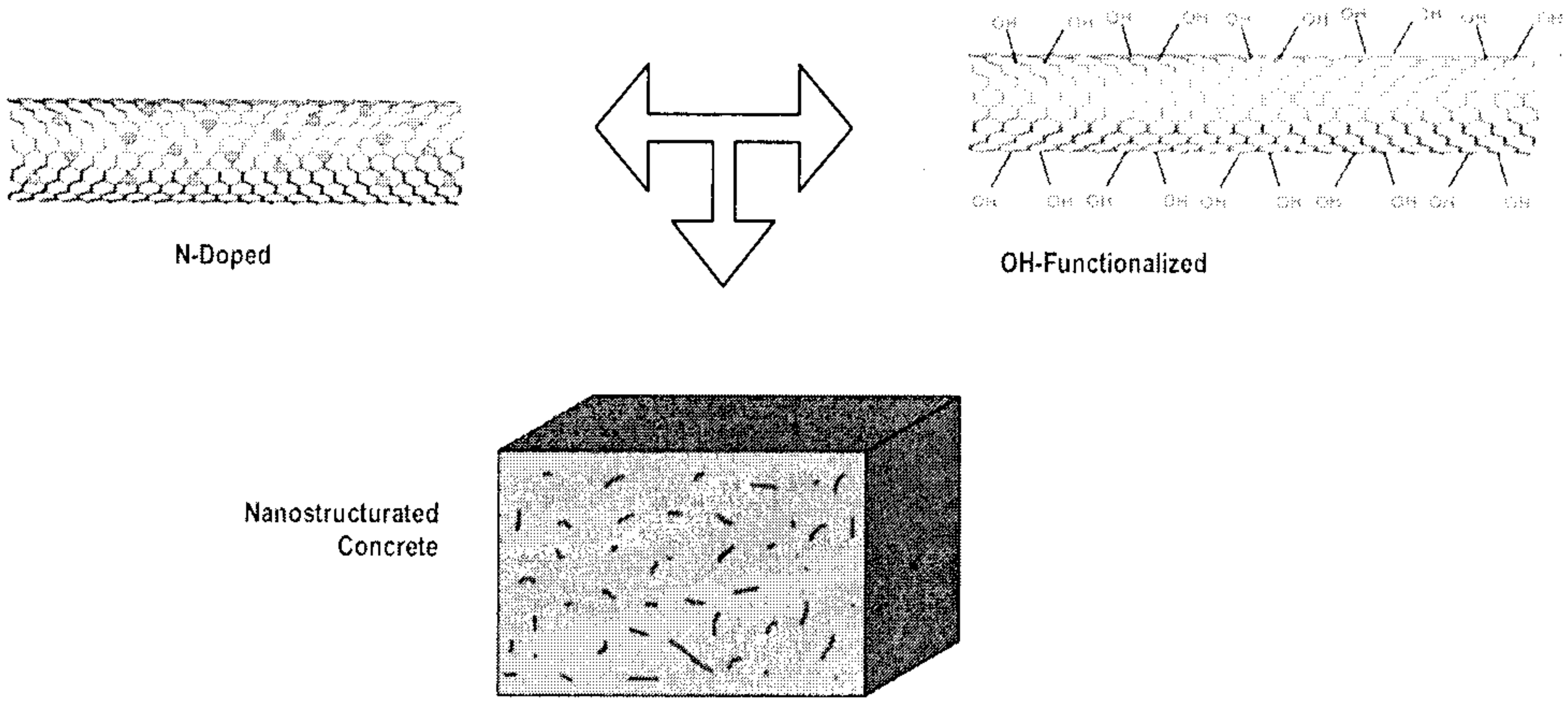


Fig. 6

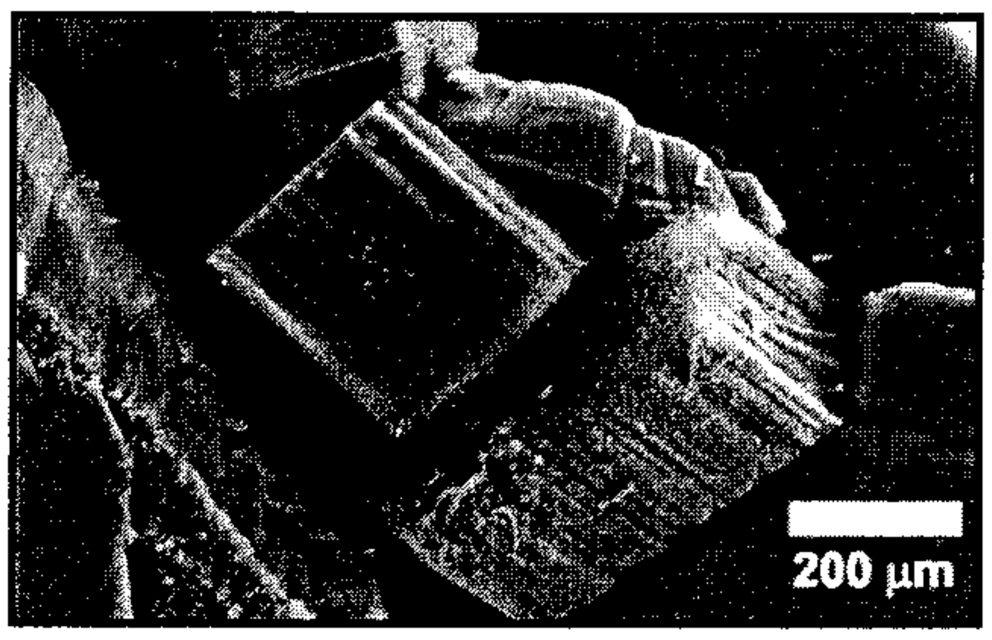


Fig. 7a

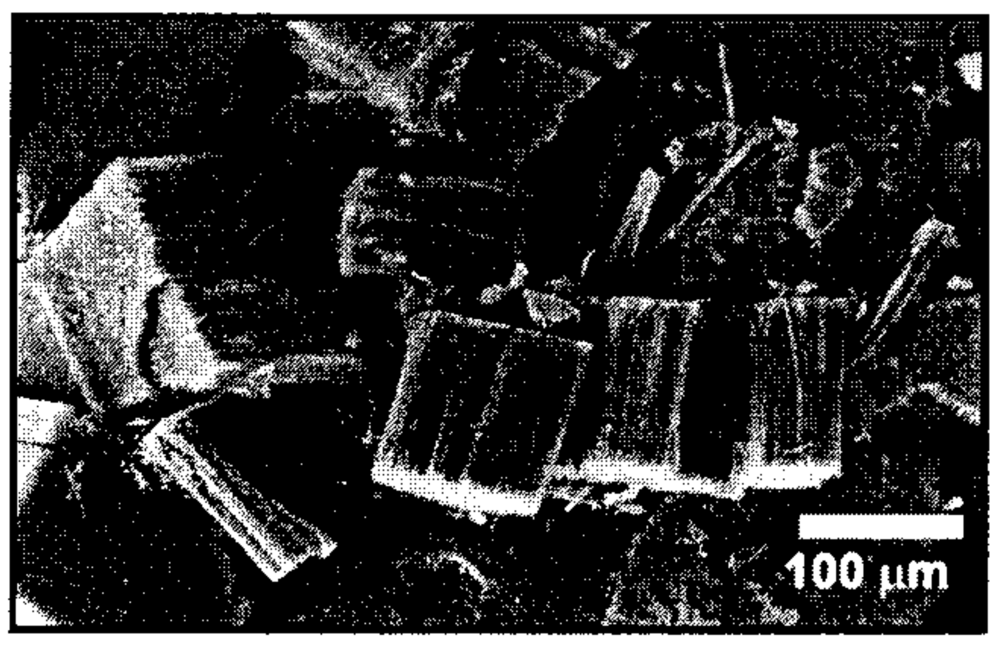


Fig. 7b

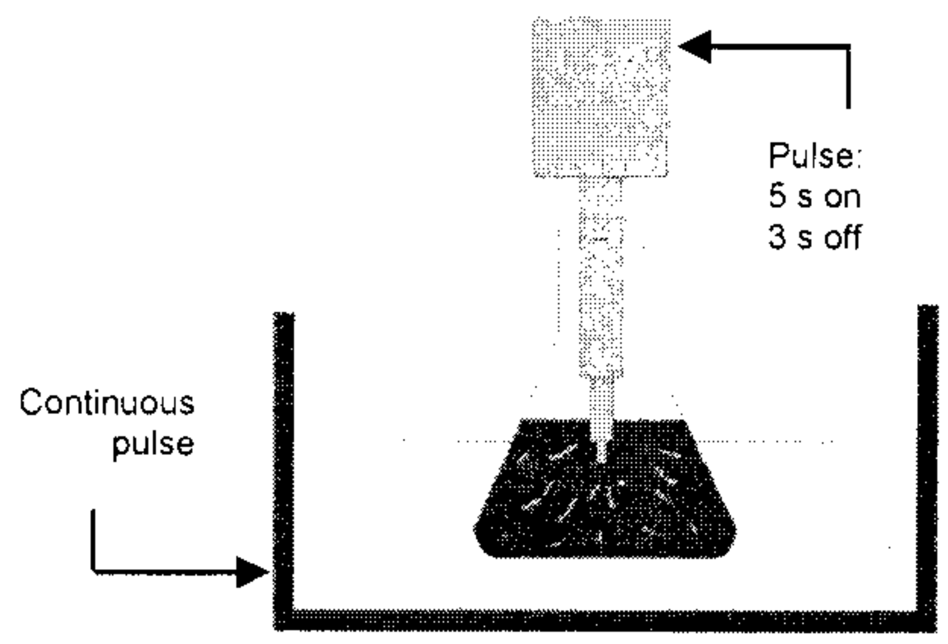


Fig. 8a

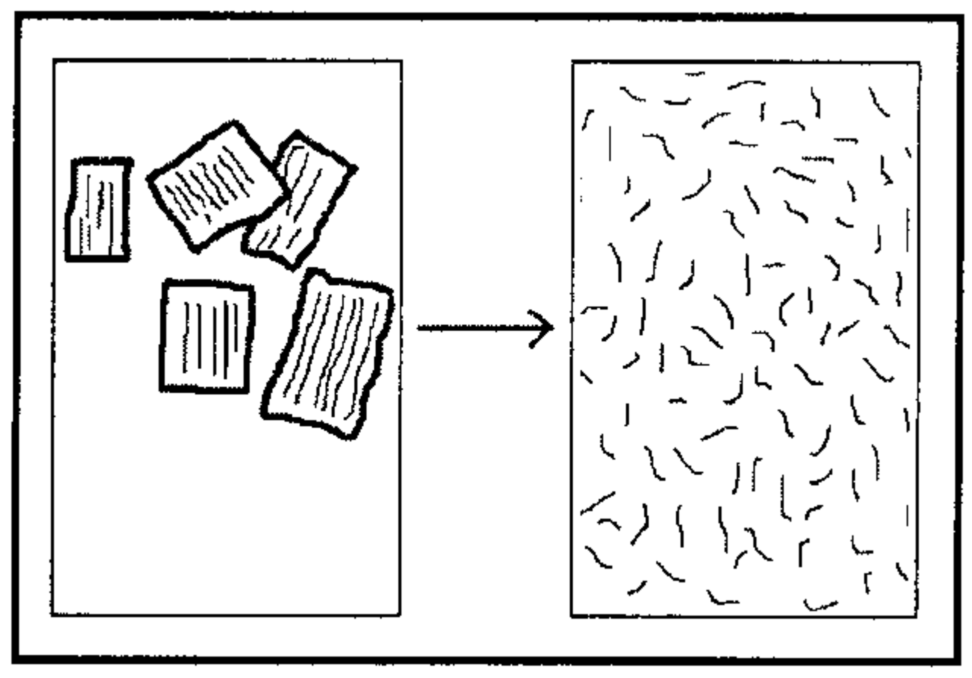


Fig. 8b

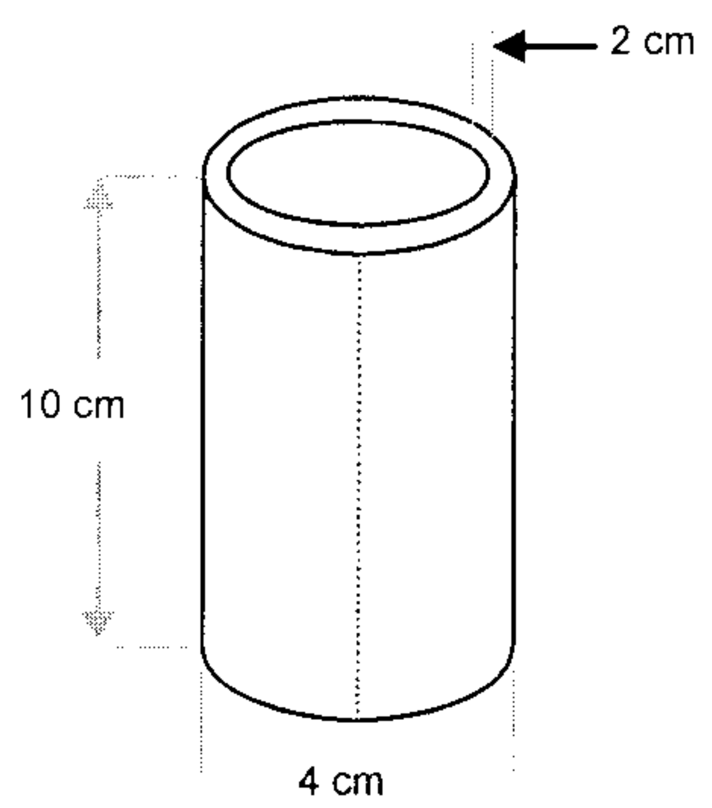


Fig. 9a

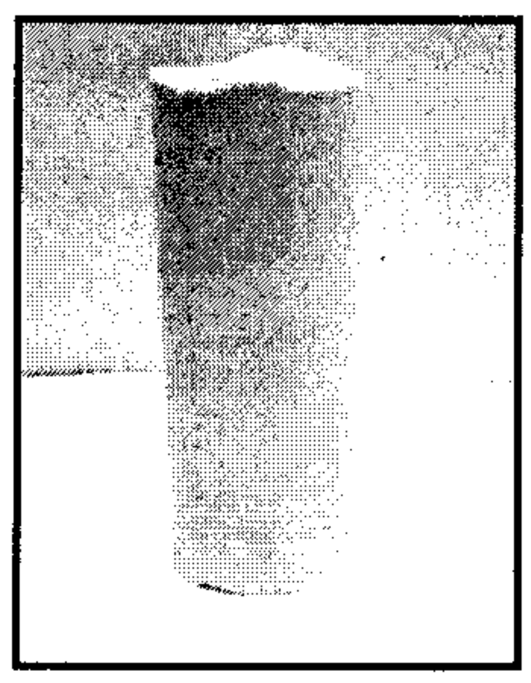
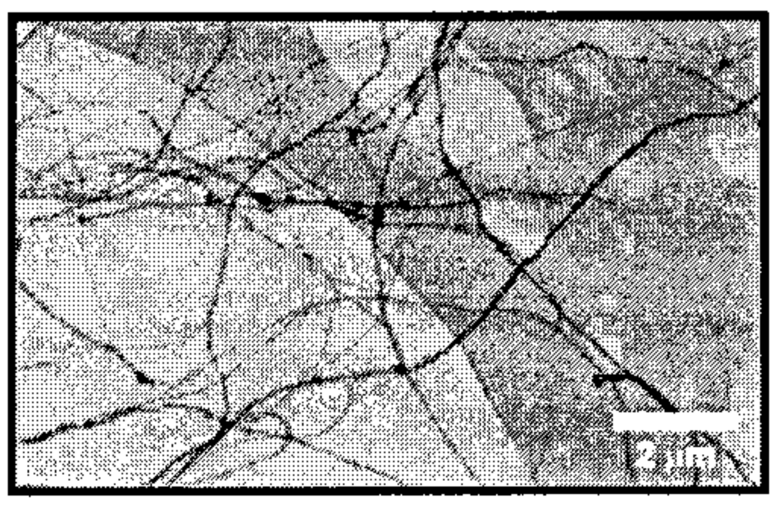
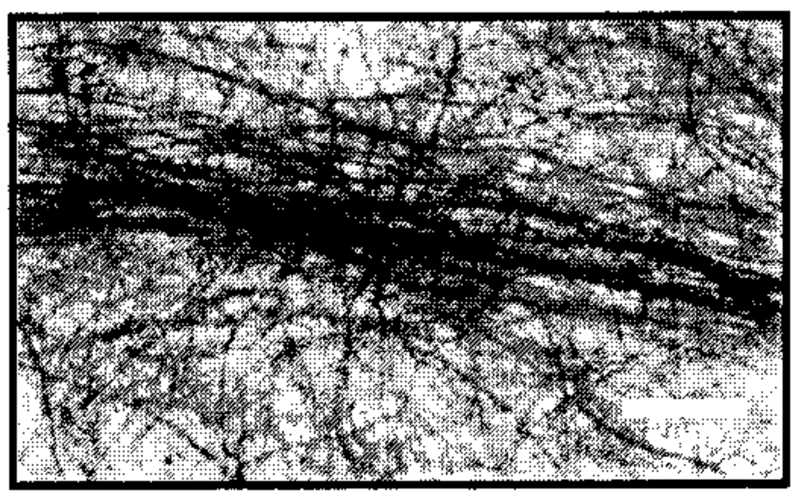
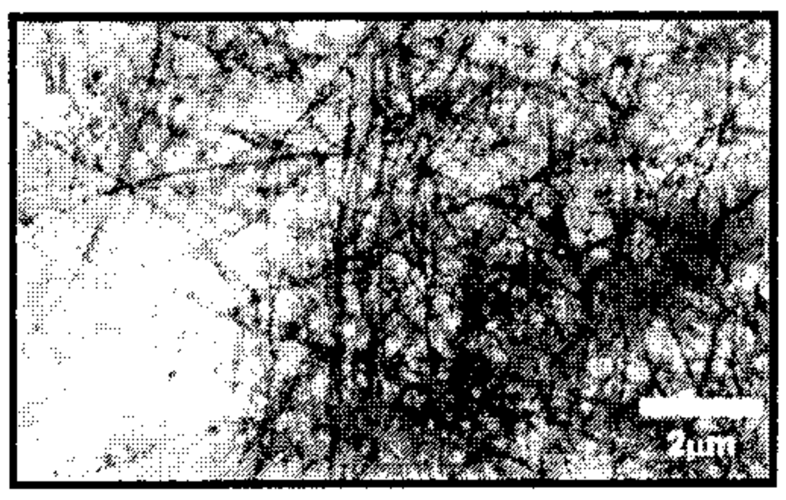


Fig. 9b



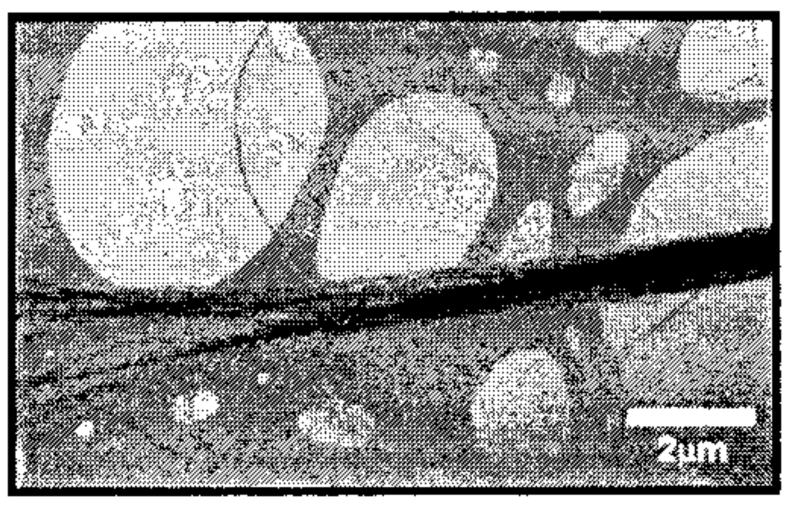




Functionalized CNT 0.01 %

Functionalized CNT

Functionalized CNT



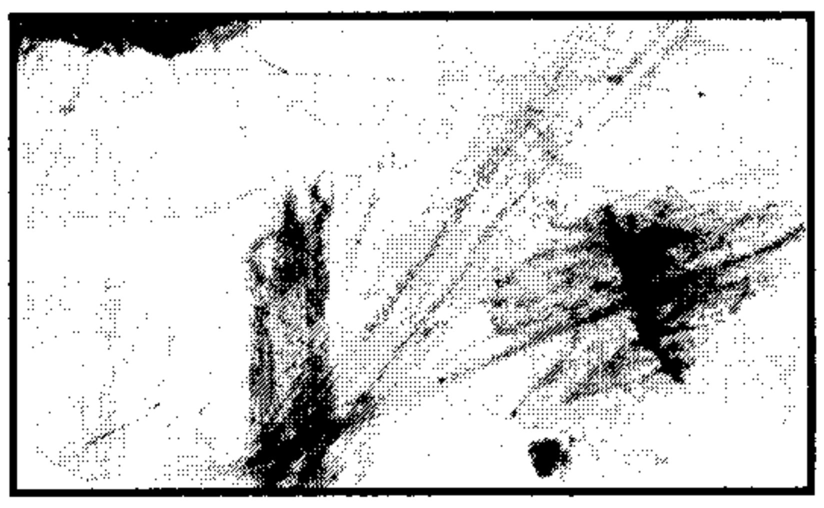


Fig. 10a

Fig. 10b

Fig. 10c

Fig. 11a

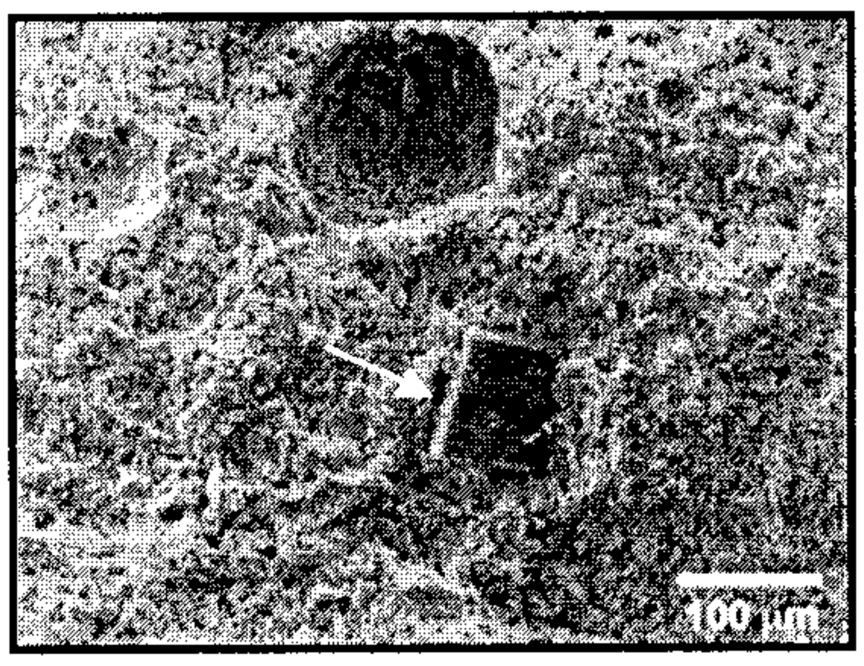


Fig. 11b

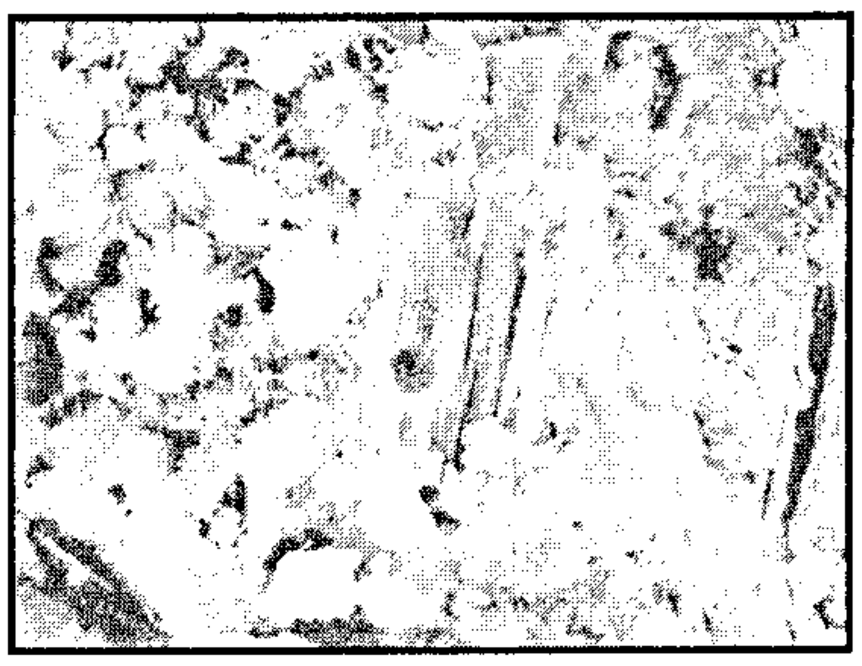


Fig. 11c

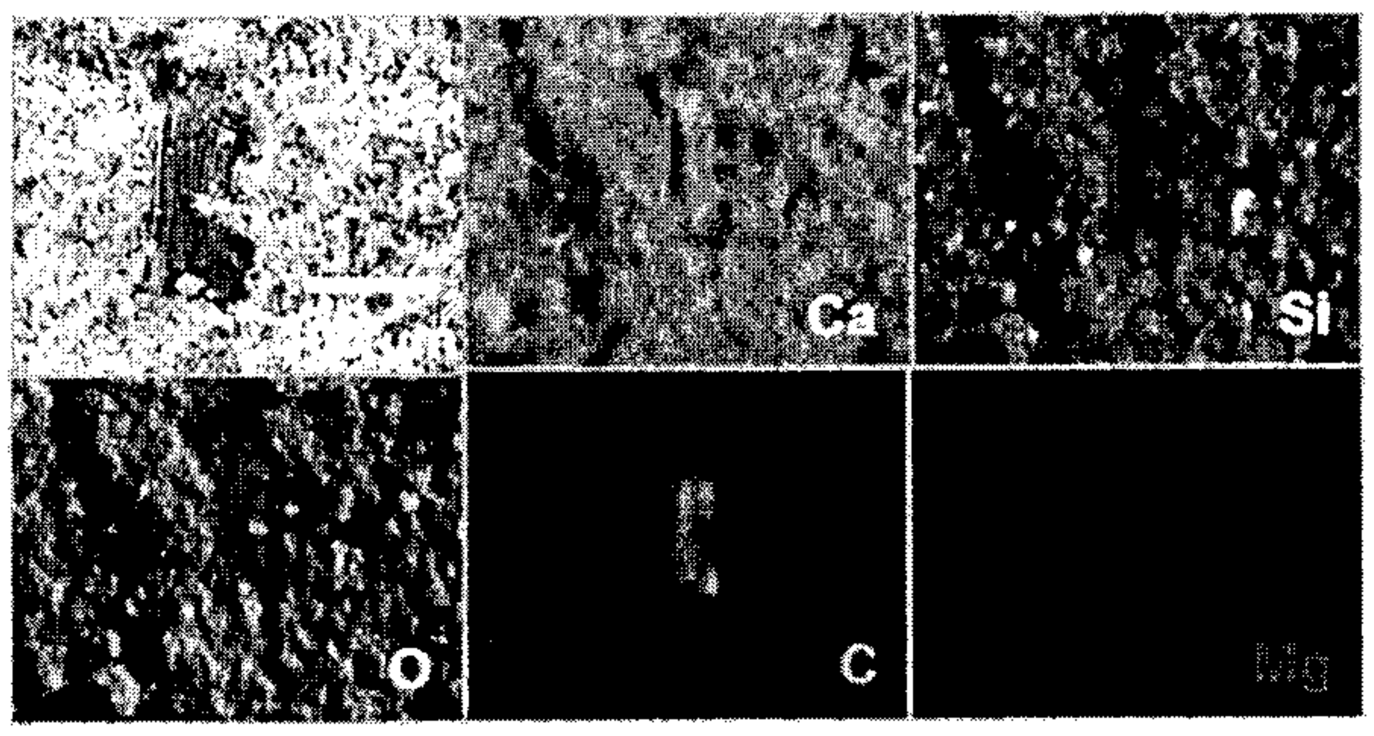
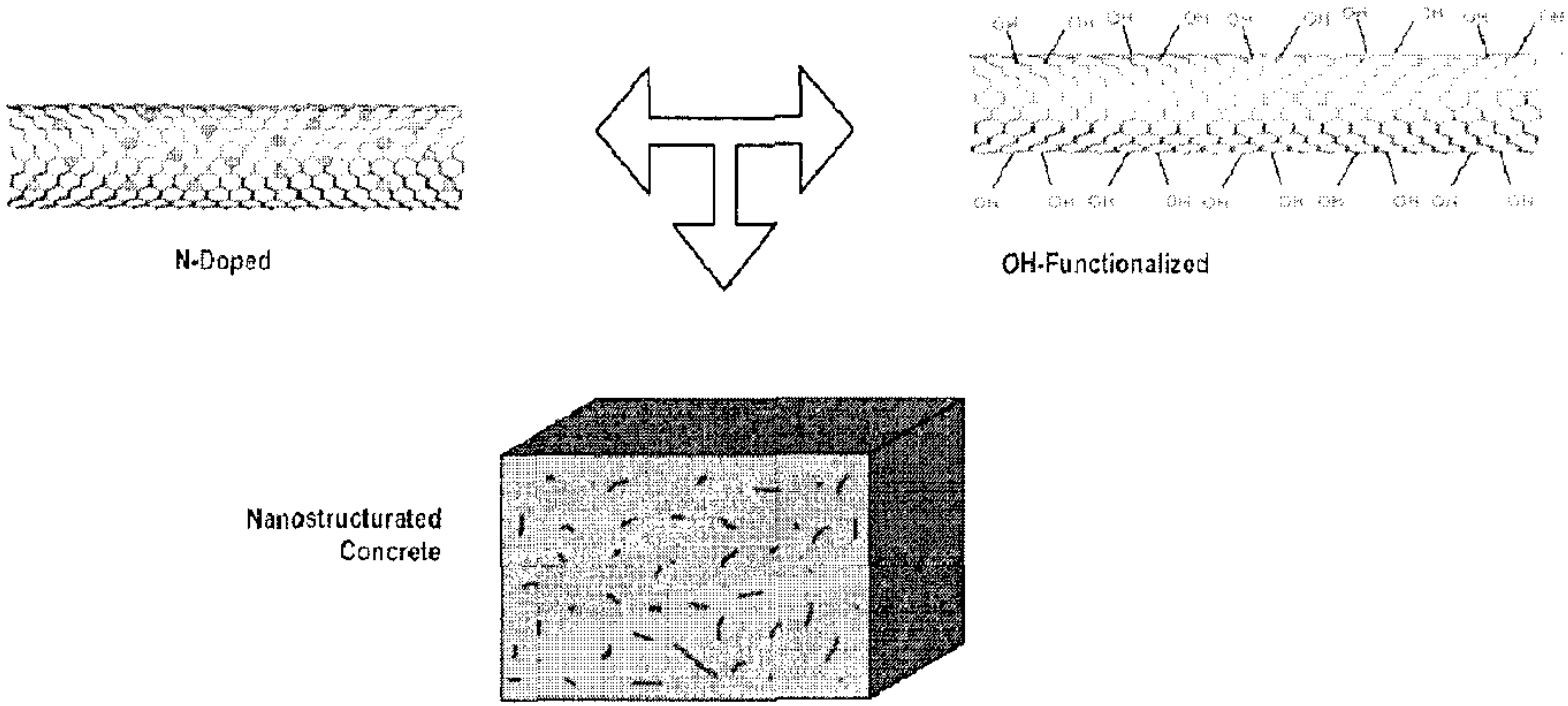


Fig. 11d


N-Doped
OH-Functionalized
Nanostructurated
Concrete