



- (51) International Patent Classification:
B01J 20/16 (2006.01)
- (21) International Application Number:
PCT/IB20 12/002885
- (22) International Filing Date:
20 November 2012 (20.11.2012)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
4062/CHE/2011 24 November 2011 (24.11.2011) IN
- (71) Applicant: INDIAN INSTITUTE OF TECHNOLOGY [IN/IN]; lit P.O., Chennai, Tamil Nadu 600 036 (IN).
- (72) Inventors: PRADEEP, Thalappil; C4, Third Loop Road, IIT Campus, Chennai, Tamil Nadu 600036 (IN). ANNAMALAI, Leelavathi; D/o A. Annamalai, 46, Muthugoundnpalayam, T P Palayam Post, Kanjikoval 6381 16 (IN). SANKAR, Mohan, Udhaya; 152/e, Samanthi Street, Ngo Nagar, Gundu Uppalavadi, Cuddalore, Tamil Nadu 607001 (IN). CHAUDHARY, Amrita; S24/6 - A, K.kh-b, Sarvodaya Nagar, Varanasi,uttar Pradesh 221002 (IN). ANSHUP; S/o Dr. Himanshu Mohan, Deputy Director (scert), Jbtc Campus, Nishatganj, Lucknow 226016 (IN).

- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: MULTILAYER ORGANIC-TEMPLATED-BOEHMITE-NANOARCHITECTURE FOR WATER PURIFICATION

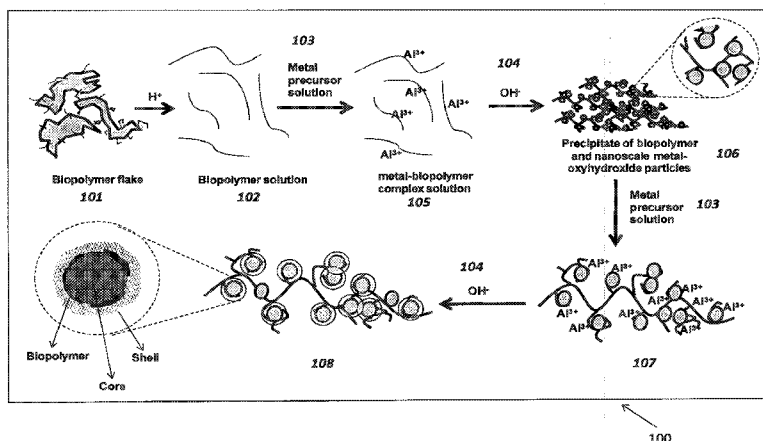


FIG. 1

(57) Abstract: An adsorbent composition comprising a nanoscale shell of metal oxide or hydroxide on an organic-templated-boehmite-nanoarchitecture (OTBN) is provided. The nanoscale shell is prepared by impregnating OTBN with a metal or a non-metal ion, followed by in-situ hydrolysis of the deposited ion on the OTBN surface. The thickness of the shell is less than about 3 nm, which is less than the size of OTBN core. The number of layers of the shell is flexible, thereby leading to a multi-layer nanoscale hybrid composition. The adsorbent composition is capable of removing inorganic anions such as fluoride from water, with an increased adsorption capacity.

WO 2013/076581 A2

MULTILAYER ORGANIC-TEMPLATED-BOEHMITE-NANOARCHITECTURE FOR WATER PURIFICATION

BACKGROUND

TECHNICAL FIELD

The present disclosure relates to the field of water purification and specifically to an organic-templated-boehmite-nanoarchitecture (OTBN) used for water purification.

TECHNICAL BACKGROUND

Availability of clean drinking water is a major health concern across the world, especially in the developing and under-developed countries. Amongst the major contaminants which contaminate water, the major ones include biological (e.g. bacteria and virus), inorganic (e.g. fluoride, arsenic, iron) and organic (e.g. pesticides, volatile organics) species. Various governmental initiatives across the world continue to support the projects to ensure availability of clean drinking water to the people of respective countries. However, it continues to be a major problem because technological costs, in many cases, continue to stay above affordable limit which eventually affects the poor as they are unable to afford clean drinking water.

The fact that poor continues to suffer due to un-availability of clean drinking water is common across various statistics collected by various sources. It is therefore important to make a technological intervention to improve the affordability of available state-of-the-art technologies. This can go a long way in improving the health of people globally.

Aluminum-based compositions have been exhaustively studied for the removal of inorganic anions, such as fluorides and arsenates from drinking water. Use of aluminum-based compositions is more pertinent for fluoride adsorption from water due to its relatively higher fluoride adsorption capacity vis-a-vis other adsorbents. Moreover, aluminum-based compositions do not require any additional pre/post-filtration. Various improvements in the capacity of aluminum-based compositions have been proposed till

date. Practically, all aluminum-based compositions in the field use require frequent regeneration, largely to reduce the cost of water purification. However, traditionally followed practice of regeneration, i.e., alkali treatment followed by acidification, leads to secondary contamination of water sources caused due to high fluoride concentration in the sludge, leaching of aluminum in water and high dissolved salt content of the sludge. Prior art related to fluoride removal using aluminum-based compositions and associated challenges are covered in detail in our previous Indian patent application 1529/CHE/2010, entire contents of which are herein incorporated by reference.

The Indian patent application 1529/CHE/2010 describes a method to produce aluminum oxyhydroxide-chitosan composite at room temperature. There are a number of advantages in the adsorbent composition, including green chemistry based preparation at room temperature, binder free granulation, ease of filter-ability/wash-ability and an easy-to-adapt method for preparation of mixed metal hydroxides/oxides.

It was reported that an adsorbent dose of 500 mg/L is sufficient to remove fluoride concentration below 0.5 ppm, when input fluoride is varied from 1-10 mg/L. The aluminum oxyhydroxide-chitosan composite exhibits a fluoride adsorption capacity of over 53 mg/g at an initial fluoride concentration of 10 mg/L in deionized water. Owing to the presence of competing anions in ground water, the fluoride adsorption capacity of the composition diminishes and an adsorbent dose of 1.5 g/L is required to remove fluoride concentration below 0.5 ppm, when input fluoride concentration in ground water is varied from 1-10 mg/L. Cost of the material is approximately Indian Rupees 350 per kg. This translates to a material cost of Indian Rupees 5 per 10L (assuming a household requires 10L of fluoride free drinking water per day).

Further, the following prior art documents have attempted to develop various fluoride removal techniques using aluminum and/or chitosan based compositions:

1. Miretzky P., Cirelli A. F., Fluoride removal from water by chitosan derivatives and composites: A review, Journal of Fluorine Chemistry 132 (201 1) 231-240;

2. Jagtap S., Yenkie M. K., Das S., Rayalu S., Synthesis and characterization of lanthanum impregnated chitosan flakes for fluoride removal in water, *Desalination* 273 (201 1) 267-275;
3. Fluoride removal from water by adsorption—A review, Bhatnagar A., Kumar E., Mika SiSlanpiS M., *Chemical Engineering Journal*, 171 (201 1) 811-840; and
4. Liu R., Gong W., Lan H., Gao Y., Liu H., Qu J., Defluoridation by freshly prepared aluminum hydroxides, 175 (201 1) 144-149.

While the prior art methods and compositions are effective in fluoride removal from water to a large extent, there exists a scope for improvement. For example, even the reduced cost of the adsorbent composition is still too high for some of the Indian households. Mainly, it is expected that the water purification composition satisfies the following conditions:

Firstly, the adsorbent composition should be implementable at the household level, *i.e.*, it should exhibit high adsorption kinetics and low empty bed contact time. Secondly, the adsorbent composition should require no regeneration, and thus should not generate any secondary contamination. Thirdly, the adsorbent composition should be easy-to-use and maintain, *i.e.*, it should not require any pre/post-filtration. Fourthly, the adsorbent dose should be able to reduce any input concentration that is below 10 ppm to below 1 ppm, as per the Indian National Sanitation Foundation norm for water to be used for fluoride removal. Finally and most importantly, the cost of water purification should not exceed Indian Rupees 3 per 10 L of purified water (*i.e.*, the composition should be affordable) and the quantity of adsorbent should not exceed 2-3 g per 10 L of purified water.

In light of the foregoing discussion, there exists a need to address the aforementioned problems and other shortcomings associated with the prior art methods and compositions. These needs and other needs are satisfied by the water purification composition of the present disclosure. Considering the widespread contamination of fluoride across the globe, the water purification composition of the present invention will have a major positive effect on the health of the society as it can be used to provide point-of-use water filters.

SUMMARY

In accordance with the purpose(s) of the invention, as embodied and broadly described herein, this disclosure, in one aspect, relates to water purification. Particularly, the disclosure relates to a nanoscale shell of metal oxide/hydroxide on an organic-templated-boehmite-nanoarchitecture.

An object of the present invention is to provide an adsorption composite that exhibits high adsorption kinetics and low empty bed contact time, and that is easily implementable at a household level.

Another object of the present invention is to provide an adsorption composite that requires no regeneration and thus has no secondary contamination.

Yet another object of the present invention is to provide an adsorbent composition that is easy-to-use and maintain, *i.e.*, the adsorption composition should not require any pre/post-filtration.

Yet another object of the present invention is to provide an adsorbent dose that is able to reduce any input concentration that is below 10 ppm to below 1 ppm.

Still another object of the present invention is minimize the cost of water purification to less than Indian Rupees 3 per 10 L of purified water, and to minimize the quantity of adsorbent to 2-3 g per 10 L of purified water.

In one aspect, an adsorbent composition for the removal of fluoride from water is provided. The adsorption composition includes a nanoscale shell of metal oxyhydroxide / hydroxide / oxide on organic-templated-boehmite-nanoarchitecture (OTBN, referred to as 'core'). The size of the shell is less than about 3 nm, which exhibits high anion adsorption capacity from water. Preparation of nanoscale metal hydroxide of size less than about 3 nm is achieved by precipitation of metal ion on the surface of OTBN. Highest fluoride adsorption capacity is achieved when weight ratio of aluminum in shell to aluminum in

core (A_{shell}:A_{core}) reaches 90%. Consequently, a 100% improvement in the fluoride adsorption capacity is reported vis-a-vis OTBN.

In another aspect, an adsorbent dose of 0.75 g/L is required to remove fluoride concentration below 0.5 ppm, when input fluoride concentration in ground water is varied from 1-10 mg/L. This translates to a material cost of Indian Rupees 2.5 per 10 L of water; leading to 50% reduction in the material cost vis-a-vis earlier reported compositions.

In one aspect, a granular composite of nanoscale multi-layer metal oxyhydroxide ("shell") on OTBN ("core") is provided. The granular composite is prepared by formation of multi-layer on OTBN in gel form. In another aspect, the granular composite is prepared by the formation of a multi-layer on OTBN in the solid form.

In another aspect, the present disclosure provides a method for preparation of nanoscale metal oxide / hydroxide / oxyhydroxide shell on OTBN. In a general aspect, the method includes contacting a metal precursor with the OTBN in gel state in aqueous medium and then contacting the resulting mixture with a base. In another aspect, the metal precursor in the aqueous medium is contacted with OTBN in the solid state and the resulting mixture is contacted with a base.

In various aspects, the metal precursor includes a salt of a metal or a solution thereof. In various aspects, the metal component includes aluminum, iron, titanium, manganese, cobalt, nickel, copper, silver, zinc, lanthanum, cerium, zirconium, calcium, magnesium, barium, or a combination thereof. In another aspect, the metal precursor includes a solution of an aluminum salt that includes aluminum sulfate. In another aspect, the metal precursor includes a solution of an aluminum salt that includes aluminum nitrate, aluminum acetate, aluminum chloride, aluminum isopropoxide, or a combination thereof. In another aspect, the metal precursor includes a mixture of two or more individual metal precursors in any desired ratio, such as, for example, from about 20:1 to about 1:20, and for example, about 20:1, 10:1, 5:1, 2:1, 1:1, 1:2, 1:5, 1:10, and 1:20.

The base used in the hydrolysis of metal precursor may include any suitable base, such as sodium hydroxide, ammonia, potassium hydroxide, or a combination thereof. In other

aspects, other bases or combination of bases and/or solutions thereof can be used, and the present invention is not intended to be limited to a particular base. In one aspect, upon addition of the base to a mixture of metal precursor and OTBN, metal ions hydrolyze and precipitate in the form of a nanoscale layer on OTBN surface. Upon precipitation of metal precursor with the base, a semi-solid precipitate including nanoscale metal hydroxide / oxide / oxyhydroxide shell on OTBN is formed. In one aspect, the thickness of the resulting shell layer is in the range of about 1 nm to about 10 nm. In another aspect, the thickness of the resulting shell layer is in the range of from about 1 nm to about 5 nm. The semi-solid precipitate is typically subjected to filtration and washing with copious amounts of water followed by drying to obtain the desired granular composite.

In various aspects, the present invention provides methods for preparing nanoscale shell of metal oxide/hydroxide on OTBN. In another aspect, the composition can be used for the removal of inorganic anions from drinking water such as arsenic and fluoride.

Additional aspects and advantages of the invention will be set forth, in part, in the detailed description and any claims which follow, and in part will be derived from the detailed description or can be learned by practice of the invention. The advantages described below will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention as disclosed.

BRIEF DESCRIPTION OF THE FIGURES

The accompanying figures, which are incorporated in and constitute a part of this specification, illustrate several aspects and together with the description serve to explain the principles of the invention.

FIG. 1 is a schematic representation of chemical reactions involved in the method for preparation of composition, in accordance with an aspect of the present invention.

FIG. 2 depicts XRD patterns of (a) as-synthesized parent material OTBN (indexed to the standard reflections of AlOOH (JCPDS 21-1307)), (b) nanoscale aluminum hydroxide coated OTBN (ratio of Al content in shell to Al content in OTBN = 0.45) and (c) nanoscale aluminum hydroxide coated on OTBN (ratio of Al content in shell to Al content in OTBN = 0.9), in accordance with an aspect of the present invention.

FIG. 3 depicts TEM image of nanoscale aluminum hydroxide coated on OTBN, in accordance with an aspect of the present invention.

FIG. 4 depicts XPS survey spectra of (a) nanoscale aluminum hydroxide coated OTBN and (b) nanoscale aluminum hydroxide coated OTBN exposed to 100 mg/L fluoride that confirms the existence of adsorbed fluoride along with disappearance of sulfate ion in the F treated composition, in accordance with an aspect of the present invention.

FIG. 5 depicts XPS spectra of (A) Al 2p, (B) O 1s, (C) F 1s and (D) S 2p, for adsorbent composition (a) before and (b) after exposure to 100 mg/L fluoride, in accordance with an aspect of the present invention.

FIG. 6 depicts EDAX spectrum of nanoscale aluminum hydroxide coated OTBN, wherein the inset shows elemental X-ray images of Al Ka, O Ka, C Ka and S Ka of the sample, corresponding SEM image, and elemental quantification, in accordance with an aspect of the present invention.

FIG. 7 depicts EDAX spectrum of nanoscale aluminum hydroxide coated OTBN after exposure to 100 mg/L fluoride with 5 mg adsorbent dose (in deionized water), wherein the inset shows elemental X-ray images of Al Ka, O Ka, C Ka, F Ka and S Ka of the sample, corresponding SEM image, and elemental quantification, in accordance with an aspect of the present invention.

FIG. 8 depicts (a) adsorption capacity of OTBN, and (b) adsorption capacity of nanoscale aluminum hydroxide coated OTBN as function of adsorbent dose in de-ionized water (initial fluoride concentration = 10 mg/L), in accordance with an aspect of the present invention.

FIG. 9 depicts adsorption capacity of nanoscale aluminum hydroxide coated OTBN as a function of varying aluminum content in nanoscale shell vis-a-vis aluminum content in the core (initial fluoride concentration = 10 mg/L, ground water), in accordance with an aspect of the present invention.

DESCRIPTION

The present invention can be understood more readily by reference to the following detailed description of the invention and the examples included therein.

Before the present compounds, compositions, articles, systems, devices, and/or methods are disclosed and described, it is to be understood that they are not limited to specific synthetic methods unless otherwise specified, or to particular reagents unless otherwise specified, as such can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, example methods and materials are now described.

All publications mentioned herein are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited.

DEFINITIONS

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, example methods and materials are now described.

As used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a metal" includes mixtures of two or more metals.

Ranges can be expressed herein as from "about" one particular value, and/or to "about" another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as "about" that particular value in addition to the value itself. For example, if the value "10" is disclosed, then "about 10" is also disclosed. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

As used herein, the terms "optional" or "optionally" means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

Disclosed are the components to be used to prepare the compositions of the invention as well as the compositions themselves to be used within the methods disclosed herein. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds cannot be explicitly disclosed, each is specifically contemplated and described herein. For example, if a particular compound is disclosed and discussed and a number of modifications that can be made to a number of molecules including the compounds are discussed, specifically contemplated is each and every combination and permutation of the compound and the modifications that are possible unless specifically indicated to the contrary. Thus, if a class of molecules A, B, and C are disclosed as well as a class of molecules D, E, and F and an example of a

combination molecule, A-D is disclosed, then even if each is not individually recited each is individually and collectively contemplated meaning combinations, A-E, A-F, B-D, B-E, **B-F**, C-D, C-E, and C-F are considered disclosed. Likewise, any subset or combination of these is also disclosed. Thus, for example, the sub-group of A-E, B-F, and C- E would be considered disclosed. This concept applies to all aspects of this application including, but not limited to, steps in methods of making and using the compositions of the invention. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific embodiment or combination of embodiments of the methods of the invention.

Each of the materials disclosed herein are either commercially available and/or the methods for the production thereof are known to those of skill in the art.

It is understood that the compositions disclosed herein have certain functions. Disclosed herein are certain structural requirements for performing the disclosed functions and it is understood that there are a variety of structures that can perform the same function that are related to the disclosed structures, and that these structures will typically achieve the same result. Moreover, the result presented here should not be construed as limiting the scope of the invention.

Experimental methods

Material characterization

Identification of the phase(s) of the as-prepared samples was carried out by X-ray powder diffraction (Bruker AXS, D8 Discover, USA) using Cu-K α radiation at $\lambda = 1.5418$ **A**. High resolution Transmission Electron Microscopy (HRTEM) images of the sample were obtained with JEM 3010 (JEOL, Japan). The samples prepared as above were spotted on amorphous carbon films supported on copper grids and dried at room temperature. X-ray Photoelectron Spectroscopic (XPS) analysis was carried out by using ESCA Probe TPD of Omicron Nanotechnology. Polychromatic Mg Ka was used as the X-ray source ($h\nu = 1253.6$ eV). Spectra in the required binding energy range were collected and an average was taken. Beam induced damage of the sample was reduced

by adjusting the X-ray flux. Binding energy was calibrated with respect to C 1s at 284.5 eV. Surface morphology, elemental analysis and elemental mapping studies were carried out using a Scanning Electron Microscope (SEM) equipped with Energy Dispersive Analysis of X-rays (EDAX) (FEI Quanta 200). The sample was re-suspended in water by sonication for 10 min and drop casted on an indium tin oxide (ITO) conducting glass and dried.

Adsorption studies

The adsorbent composition was tested for fluoride (in the form of NaF) removal from water. All uptake capacity studies were performed in a batch reactor (250 ml polypropylene conical flask). The working volume of the solution was taken as 100 ml and required quantity of adsorbent was added. The flasks were kept for shaking at 160 ± 5 rpm in an orbital shaker at room temperature. Samples were withdrawn at duration of 1.5 hour and analyzed for residual solute concentration.

The water used for studies was either deionized water or tap water (composition is mentioned herewith), and it is mentioned in the respective figures and the forthcoming description.

EXAMPLES

The present application describes the methods for preparing nanoscale shell of metal oxide/hydroxide on OTBN. The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices and/or methods claimed herein are made and evaluated, and are intended to be purely exemplary of the invention and are not intended to limit the scope of what the inventors regard as their invention.

Example 1

This example describes the formation of aluminum hydroxide as a nanoscale layer on OTBN. OTBN was prepared as reported in the previous Indian patent application

1529/CHE/2010, entire contents of which are herein incorporated by reference. The OTBN gel obtained after washing the salt content was used for the formation of a nanoscale layer thereover. The OTBN gel was re-dispersed in water, to which aluminum precursor, such as aluminum sulfate was added drop-wise. The ratio of Al in the shell to Al in the core may be varied anywhere between 0.5-300%. After stirring the solution for 2 hours, aqueous sodium hydroxide (2 M NaOH) was added to the solution drop-wise so that the metal precursor was hydrolyzed. Then the solution was allowed to stir for half an hour, filtered, and washed with copious amounts of water. The obtained gel was then dried at room temperature for further studies.

Example 2

This example describes the formation of nanoscale multilayer metal oxide/hydroxide on OTBN, in accordance with an aspect of the present invention. 0.2 M aluminum precursor solution was slowly added to a diluted chitosan solution (0.75 g/L) with vigorous stirring for 60 minutes and was kept overnight without agitation. Thereafter, aqueous 2 M NaOH was slowly added in to the metal-chitosan solution with vigorous stirring to facilitate the precipitation of the metal-chitosan composites. The steps were carried out at a temperature below 30 °C. The precipitate was filtered and washed with copious amount of water. The gel was then re-dispersed in water.

Thereafter, aluminum precursor solution was added to the above solution. The ratio of Al in the shell layer to Al in the core may be varied anywhere between 0.5-300%. After stirring the solution for 2 hours, aqueous sodium hydroxide (NaOH) was added to the solution drop-wise such that metal precursor underwent hydrolysis. The solution was then allowed to stir for half an hour, filtered, and washed with copious amounts of water. The obtained gel was then dried at room temperature for further studies.

Example 3

This example describes the formation of nanoscale metal oxide / hydroxide / oxyhydroxide shell on OTBN, in accordance with another aspect of the present invention. Precipitated chitosan solution was prepared by adding aqueous NaOH to chitosan

solution. Aluminum precursor solution was slowly added to the precipitated chitosan solution with vigorous stirring for 60 minutes and was kept overnight without agitation. Thereafter, aqueous 2 M NaOH was slowly added to facilitate the hydrolysis of metal precursor in precipitated chitosan matrix. The steps were carried out at a temperature below 30 °C. The precipitate was filtered and washed with copious amounts of water. The gel was then re-dispersed in water.

Thereafter, aluminum precursor solution was added to the above solution. The ratio of Al in the shell layer to Al in core may be varied anywhere between 0.5-300%. After stirring the solution for 2 hours, aqueous 2 M NaOH was added to the solution drop-wise such that metal precursor underwent hydrolysis reaction. Then the solution was allowed to stir for half an hour, filtered and washed with copious amounts of water. The obtained gel was then dried at room temperature for further studies.

Example 4

Dried OTBN powder was crushed to a particle size of 100-150 micron. The powder was stirred in the water, by using a shaker. Aluminum precursor solution was then slowly added thereto. The ratio of Al in the shell layer to Al in core may be varied anywhere between 0.5-300%. After stirring the mixture for 2 hours, aqueous 2 M NaOH was added drop-wise to hydrolyze the metal precursor. The mixture was allowed to stir for half an hour, filtered, and washed with copious amounts of water. The obtained powder was then dried at room temperature for further studies.

Example 5

This example describes the formation of a multi-layer of metal oxide/hydroxide on the core composition, in accordance with an aspect of the present invention. The composition as described in examples 1, 2 and 3 may be used, in the form of a gel or a powder. 1 M aluminum precursor was added drop-wise to the composition. After stirring the solution for an hour, 2 M NaOH was slowly added to hydrolyze the metal precursor. Subsequently, iron precursor was added drop-wise to the composition followed by hydrolysis using aqueous 2 M NaOH. The obtained composition was then filtered and

washed with copious amounts of water. The composition was dried at room temperature for further studies.

If the core composition is designated as A, shell 1 composition is designated as B, shell 2 composition is designated as C, it will be apparent to those skilled in the art that compositions designated as AB, ABC, ACB, ABAB, ABCABC, or combinations thereof can be prepared by the steps described in this invention.

Example 6

This example describes the formation of multi-element multi-layer OTBN, in accordance with an aspect of the present invention. The composition as described in examples 1, 2 and 3 may be used, either in form of a gel or a powder. A homogeneous solution containing 0.5 M aluminum sulfate and 0.5 M ferric sulfate was added drop-wise to the composition. After stirring the solution for an hour, 2 M NaOH was slowly added to hydrolyze the metal precursors. The obtained composition was filtered and washed with copious amounts of water. The composition was dried at room temperature for further studies.

Example 7

This example describes the formation of ferric hydroxide as a nanoscale layer on the OTBN, in accordance with an aspect of the present invention. Methods of preparation as detailed in examples 1, 2 and 3 were used, wherein an iron(III) precursor, such as ferric sulfate was used. Subsequently, the metal precursor was hydrolyzed. Semi-solid precipitate was filtered, washed with copious amounts of water, and dried for further use.

Referring now to FIG. 1, a schematic representation of chemical reaction 100 involved in the method for preparation of composition, in accordance with an aspect of the present invention, is shown. A granular composite of OTBN is obtained through the reaction 100. The reaction 100 is initiated by preparing a biopolymer solution 102 of a biopolymer flake 101. Subsequently, a metal precursor solution 103 is added to the biopolymer solution 102 to obtain a metal-biopolymer complex solution 105. A base 104 is added to the

metal-biopolymer complex solution 105 to obtain the composite of biopolymer and nanoscale metal-oxyhydroxide particles. Eventually, a semi solid precipitate 106 that includes nanoscale metal-oxyhydroxide particles aligned on chitosan is obtained, which is subsequently washed with copious amounts of water.

The filtered composite gel 106 is homogeneously dispersed in distilled water. Metal precursor solution 103 is then added to metal oxyhydroxide particles-biopolymer composite 106. Metal oxyhydroxide particles-biopolymer composite 106 and metal ions of metal precursor solution 103 interact with each other through a number of functional groups to obtain metal ion complexed metal oxyhydroxide particles-biopolymer composite 107. Further, a base 104 is added to the metal oxyhydroxide particles-biopolymer composite 107. Upon addition of the base 104, metal ions 103 hydrolyze and precipitate on metal oxyhydroxide particles-biopolymer composite 106 as core-shell particles. Eventually, a semi solid precipitate 108 that includes core-shell particles aligned on chitosan matrix is obtained. The precipitate 108 is washed with copious amounts of water and is dried at a temperature between 30-60 °C.

FIG. 2 depicts XRD patterns of (a) as-synthesized parent material OTBN (indexed to the standard reflections of AlOOH (JCPDS 21-1307)), (b) nanoscale aluminum hydroxide coated OTBN (ratio of Al content in shell to Al content in OTBN = 0.45) and (c) nanoscale aluminum hydroxide coated on OTBN (ratio of Al content in shell to Al content in OTBN = 0.9), in accordance with an aspect of the present invention. The as-synthesized core composition showed peaks corresponding to (020), (120), (013), (200) (231) and (251) planes (FIG. 2, curve a). The peaks can be indexed as orthorhombic-AlOOH (JCPDS 21-1307). XRD pattern of nanoscale aluminum hydroxide coated OTBN is shown in FIG. 2b. Two major changes are observed in the patterns of OTBN and nanoscale aluminum hydroxide coated OTBN. Peaks indexed to (031) and (200) have broadened and therefore merged; as are the peaks indexed to (231) and (251). Peak broadening may be interpreted as decreasing crystallite size and reduction in crystalline behavior of the material. The first possibility indicates the formation of a thin nanoscale shell on the surface of OTBN, wherein the particle size is extremely small. It is also possible that nanoscale shell may be amorphous in nature and due to its surface coverage, the crystalline features of OTBN are not pronounced. With the increasing

percentage of nanoscale shell, the crystalline features are even further masked, which indicates that nanoscale shell is amorphous in nature.

FIG. 3 depicts TEM image of nanoscale aluminum hydroxide coated on OTBN, in accordance with an aspect of the present invention. The formation of nanoscale shell on OTBN is evident from the images. It appears that nanoscale shell has encapsulated more than one particle. Individual OTBN particles can be observed in the images. The contrast between OTBN and nanoscale shell may be due to the differences in the focal plane.

FIG. 4 depicts XPS survey spectra of (a) nanoscale aluminum hydroxide coated OTBN and (b) nanoscale aluminum hydroxide coated OTBN exposed to 100 mg/L fluoride that confirms the existence of adsorbed fluoride along with disappearance of sulfate ion in the F- treated composition, in accordance with an aspect of the present invention. To understand the chemical changes in the composition upon adsorption of fluoride, detailed scans of specific regions of key elements (Al, 2p, O 1s, F 1s, S 2p) were carried out. Figure 5 shows the corresponding spectra of various regions of interest. These spectra confirm the existence of adsorbed fluoride along with the key elements, aluminum and oxygen. The XPS spectrum of aluminum 2p level shows a peak at 75.5 eV. Fluoride adsorption leads to a mild shift in the position of aluminum and it appears at lower binding energy; simultaneously a reduction in the surface positive charge is seen in oxygen, as a result of which 1s appears at a lower binding energy, with reduced intensity. Reduction in the intensity may be attributed to the loss of sulfate ion upon fluoride adsorption.

Sulfur is completely eliminated from the composition upon fluoride adsorption, indicating that the fluoride ion replaces the sulfate from the binding sites. Presence of sulfate is due to the use of aluminum sulfate as metal precursor and sulfate ions adsorb on the surface of aluminum hydroxide. We propose that sulfate plays an important role in protecting the sites of adsorbent composition; due to the presence of sulfate ion, other interfering ions with lower preference (such as chloride, nitrate, etc.) do not adsorb on the surface. While the number of surface sites available on the adsorbent surface is fixed and limited, there is always a competition between various ions usually found in water. Typically, the

occupation of sites by various ions depends on preference for adsorption and ion concentration. Ions, such as fluoride and arsenic typically have high preference but are found in low preference. Therefore, it is important to protect the surface sites to obtain maximum adsorption capacity. In the adsorbent composition of the present invention, this is accomplished by adsorption of sulfate ions on the surface sites. Sulfate ions are easily replaced by fluoride ions due to higher preference and therefore the adsorbent composition exhibits high fluoride adsorption capacity.

FIG. 6 depicts EDAX spectrum of nanoscale aluminum hydroxide coated OTBN, wherein the inset shows elemental X-ray images of Al Ka, O Ka, C Ka and S Ka of the sample, corresponding SEM image, and elemental quantification, in accordance with an aspect of the present invention. The S042- content in the composition is more than 15% (5% sulfur content). The adsorbed sulfate gets replaced with fluoride. This is reflected in FIG. 7 which depicts the corresponding data for nanoscale aluminum hydroxide coated OTBN upon fluoride adsorption (F-concentration = 10 ppm). Fluoride concentration in the adsorbed composition is more than 5%, whereas sulfur concentration is reduced to less than 1%. It is observed that the adsorbed fluoride concentration is excessively high and considering that it is observed at low input fluoride concentration, the composition is highly promising for fluoride removal.

FIG. 8 depicts (a) adsorption capacity of OTBN, and (b) adsorption capacity of nanoscale aluminum hydroxide coated OTBN as function of adsorbent dose in deionized water (initial fluoride concentration = 10 mg/L), in accordance with an aspect of the present invention. The working volume of the contaminated water was taken to be 100 ml and the quantity of adsorbent dose was varied between 5 mg to 25 mg. It is clear that nanoscale aluminum hydroxide coated OTBN has a significant improvement in the performance vis-a-vis OTBN. This was highlighted more significantly in the case when low adsorbent dose was used. It is expected that as the adsorbent dose increases, the concentration of fluoride in water decreases. The variation in capacity with adsorbent dose is minimal at higher doses because residual fluoride concentration is very less.

At the adsorbent dose of 5 mg, the composition of the present invention has fluoride adsorption capacity of 105 mg/g whereas OTBN has a fluoride adsorption capacity of 67

mg/g. This is not only a significant improvement in the fluoride adsorption capacity of aluminum based compounds, but it is also considerably higher than the adsorption capacity of OTBN.

FIG. 9 depicts adsorption capacity of nanoscale aluminum hydroxide coated OTBN as a function of varying aluminum content in nanoscale shell vis-a-vis aluminum content in the core (initial fluoride concentration = 10 mg/L, ground water), in accordance with an aspect of the present invention. The studies were conducted in ground water spiked with initial fluoride concentration of 10 mg/L. pH of the ground water was measured to be 7.8 and conductivity to be 640 pS/cm. Table (A) below shows the ion analysis of ground water (after spiking with fluoride):

Ion	Concentration	Ion	Concentration
Fluoride	10.6 ppm	Sodium	53.7 ppm
Chloride	86.4 ppm	Potassium	2.33 ppm
Nitrate	1.84 ppm	Magnesium	14.34 ppm
Sulfate	32.4 ppm	Calcium	28.7 ppm
Silicate	15.9 ppm		

Table (A): Ion analysis of ground water

The core composition (OTBN, shell percentage = 0%) showed fluoride adsorption capacity of 7.5 mg/g in ground water. The decrease in the fluoride adsorption capacity in ground water is due to the higher pH, which is known to reduce the capacity of aluminum based compounds and the presence of interfering anions such as silicate. Increasing the thickness of nanoscale shell (expressed as ratio of weight of Al in shell to weight of Al in core) increases the fluoride adsorption capacity and a maximum is reached at a weight ratio of $Al_{shell}:Al_{core}$ of 90%. Observed fluoride adsorption capacity is 15 mg/g. Upon further increase in the shell thickness, fluoride adsorption capacity eventually decreases. Hence, the optimum shell thickness is noted for a weight ratio of $Al_{shell}:Al_{core}$ at 90%.

In an aspect of the present invention, a method for preparing an adsorbent composition is provided. A nanoscale layer of at least one of a metal oxyhydroxide, a metal hydroxide, and a metal oxide is formed on an organic-templated-boehmite-nanoarchitecture (OTBN). The particle size of the nanoscale layer is less than about 3 nanometers. The adsorbent composition is used for removal of a fluoride from drinking

water. The method further includes hydrolysis of a metal precursor by using an alkaline medium. The metal precursor is contacted with OTBN, whereby a metal ion-OTBN complex is formed, which is contacted with a base. The precipitate formed is filtered, washed and dried.

In another aspect, a water purification system that includes a filter prepared by the method of the present invention is provided. The filter can be realized in the form of a candle, a molded porous block, a filter bed, a column, a packet, a sachet, and a bag. A skilled artisan will appreciate that such forms of filters are well known in the art and their description has been omitted so as not to obfuscate the present invention.

The described aspects are illustrative of the invention and not restrictive. It is therefore obvious that any modifications described in this invention, employing the principles of this invention without departing from its spirit or essential characteristics, still fall within the scope of the invention. Consequently, modifications of design, methods, structure, sequence, materials and the like would be apparent to those skilled in the art, yet still fall within the scope of the invention.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

What is claimed is:

1. A method for preparing an adsorbent composition, the method comprising:
forming a nanoscale layer of at least one of a metal oxyhydroxide, a metal hydroxide, and a metal oxide on an organic-templated-boehmite-nanoarchitecture (OTBN), wherein a particle size of the nanoscale layer is less than about 3 nanometers, whereby the adsorbent composition is used for removal of a fluoride from drinking water.
2. The method of claim 1 further comprising hydrolyzing a metal precursor by using an alkaline medium.
3. The method of claim 2, wherein the step of forming the nanoscale layer comprises:
contacting the metal precursor with OTBN, whereby a metal ion-OTBN complex is formed; and
contacting the metal ion-OTBN complex with a base, whereby the nanoscale layer of at least one of the metal oxyhydroxide, the metal hydroxide, and the metal oxide on the OTBN is formed.
4. The method of claim 3 further comprising filtering and washing a precipitate formed with water.
5. The method of claim 4 further comprising drying the filtered and washed precipitate to remove moisture content, wherein drying is performed at temperatures below about 60 °C, whereby a first material is formed.
6. The method of claim 5, wherein the drying includes at least one of air drying and sun drying.

7. The method of claim 5 further comprising grinding the first material, whereby particles in granular form are formed.

8. The method of claim 3, wherein the base comprises at least one of sodium hydroxide, potassium hydroxide, ammonia, and combinations thereof.

9. The method of claim 1, wherein the adsorbent composition is used for removal of at least one of a fluoride and an arsenic from the drinking water having a fluoride adsorption capacity in greater than about 100 mg/g at an initial fluoride concentration of about 10 mg/L.

10. The method of claim 1, wherein the OTBN is in form of a homogeneous aqueous dispersion, water-insoluble granules suspended in aqueous medium, and combinations thereof.

11. The method of claim 1, wherein the metal precursor comprises at least one of a salt of aluminum, iron, titanium, manganese, cobalt, nickel, copper, silver, zinc, lanthanum, cerium, zirconium, calcium, magnesium, barium, and combinations thereof.

12. The method of claim 1, wherein the metal precursor comprises aluminum sulfate.

13. The method of claim 1, wherein the metal precursor comprise at least of aluminum nitrate, aluminum chloride, aluminum isopropoxide, aluminum acetate, and combinations thereof.

14. The method of claim 1, wherein a thickness of the nanoscale layer is in the range of about 1 nm to about 10 nm.

15. The method of claim 1 further comprising hydrolyzing a non-metal precursor by using an alkaline medium in presence of the OTBN.

16. The method of claim 15, wherein the non-metal precursor comprises at least one of a salt of silicon, germanium, tellurium, gallium, indium, and combinations thereof.

17. The method of claim 1 further comprising hydrolyzing an acid soluble biopolymer by using an alkaline medium in presence of the OTBN.

18. The method of claim 17, wherein the acid soluble biopolymer comprises at least one of chitosan, nylon, and combinations thereof.

19. The method of claim 1, wherein the adsorbent composition is used in form of at least one of a candle, a molded porous block, a filter bed, a column, a packet, a sachet and a bag.

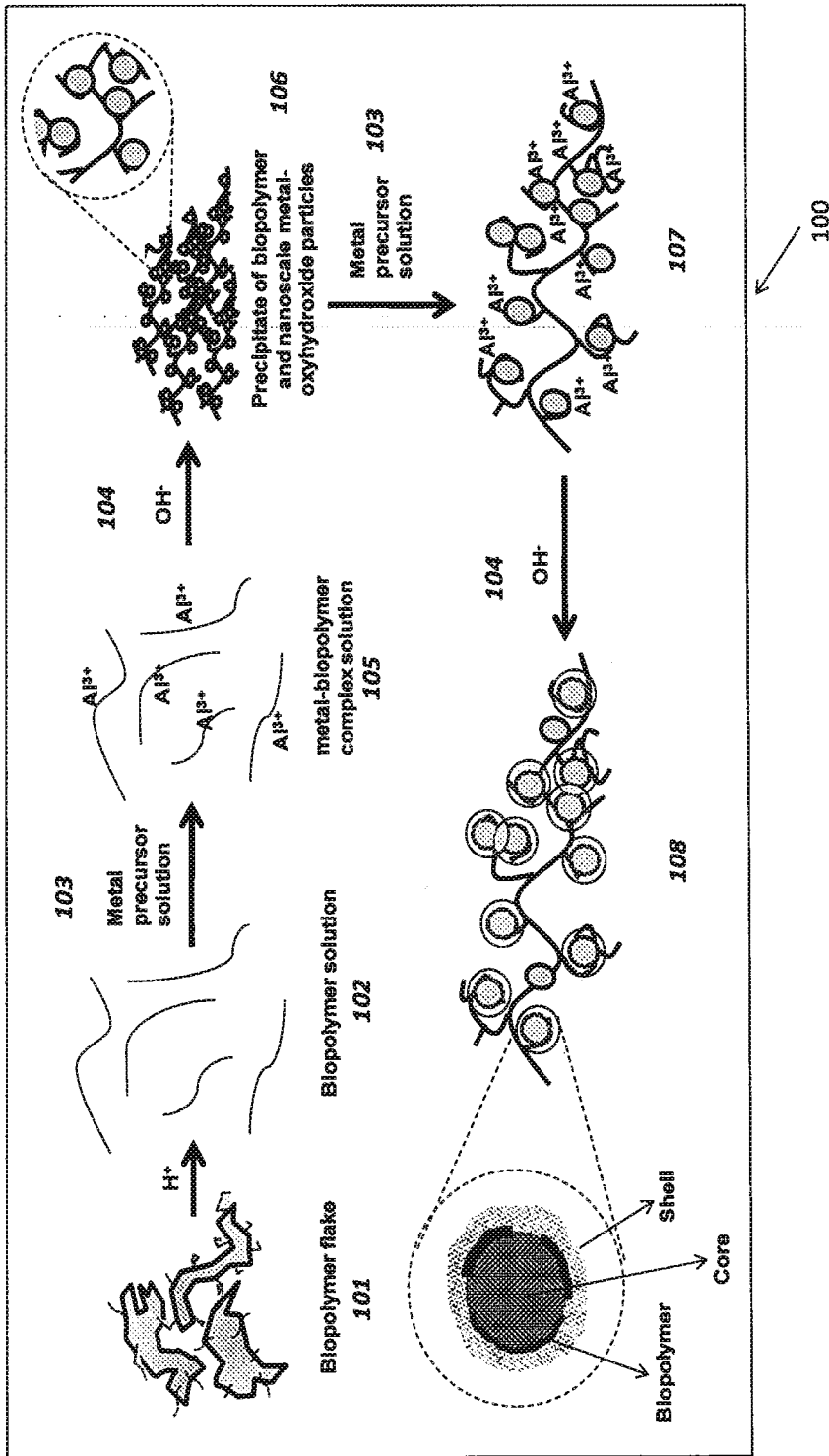


FIG. 1

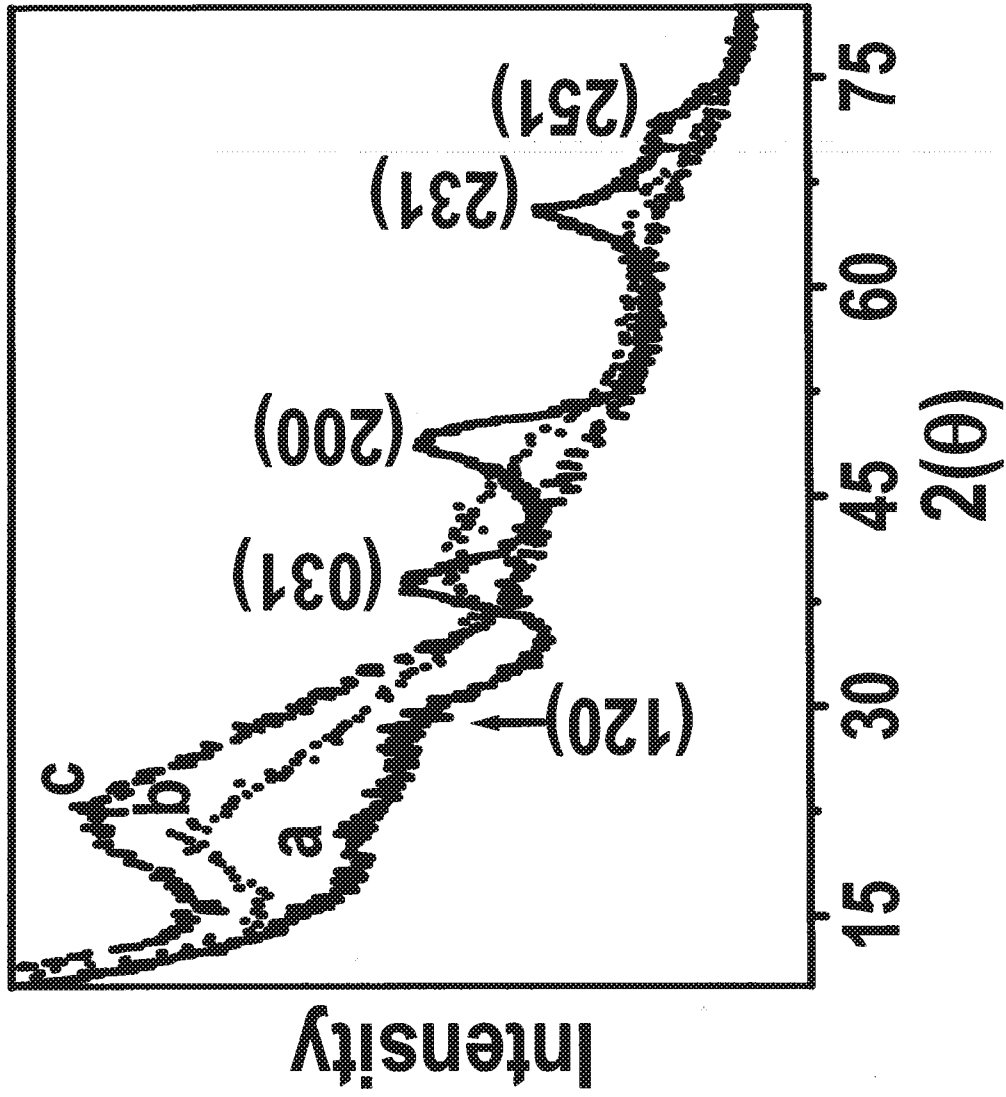


FIG. 2

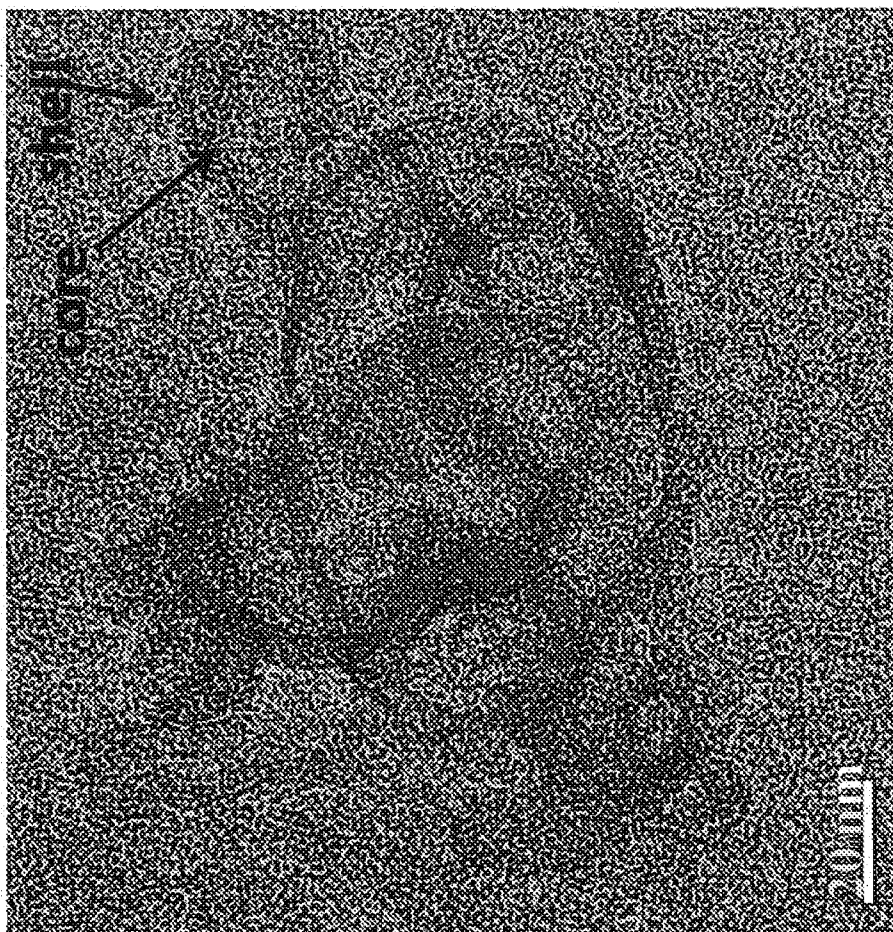


FIG. 3

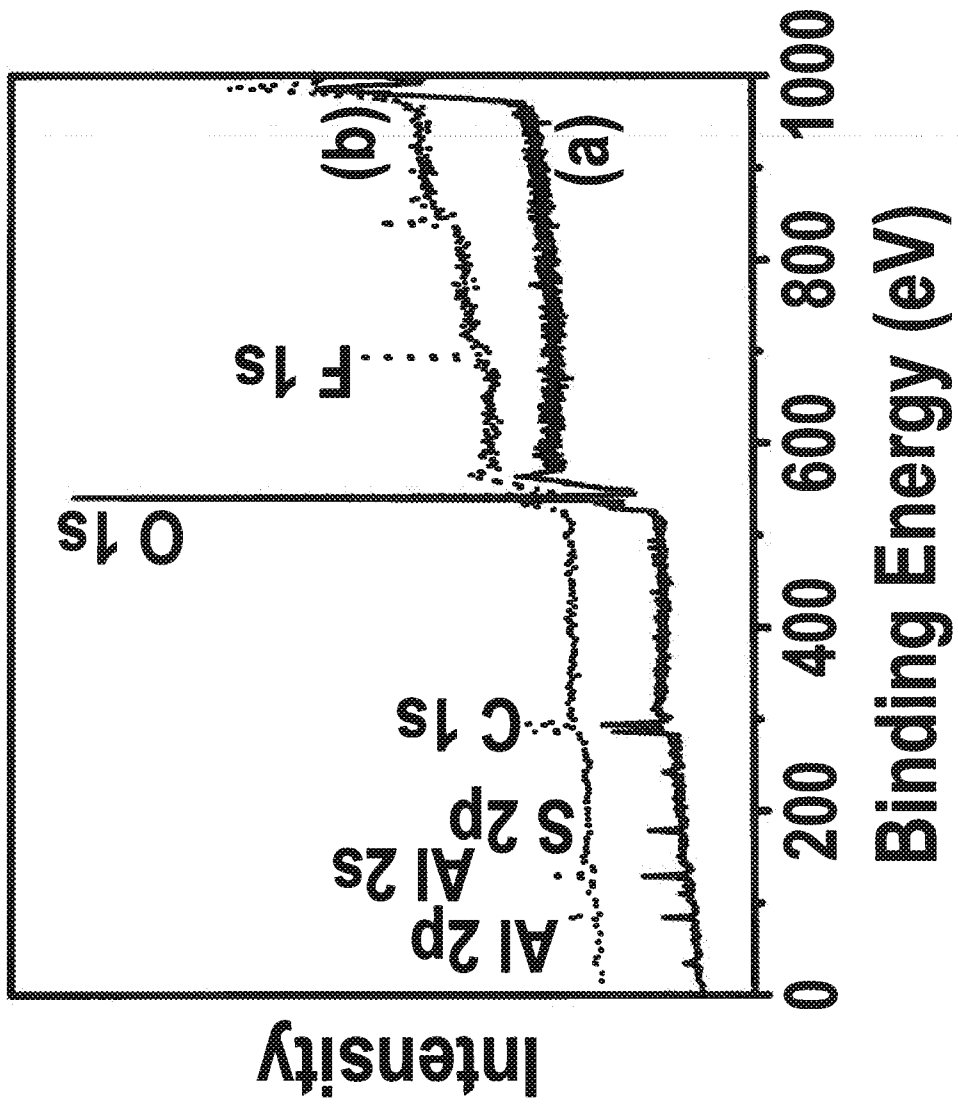


FIG. 4

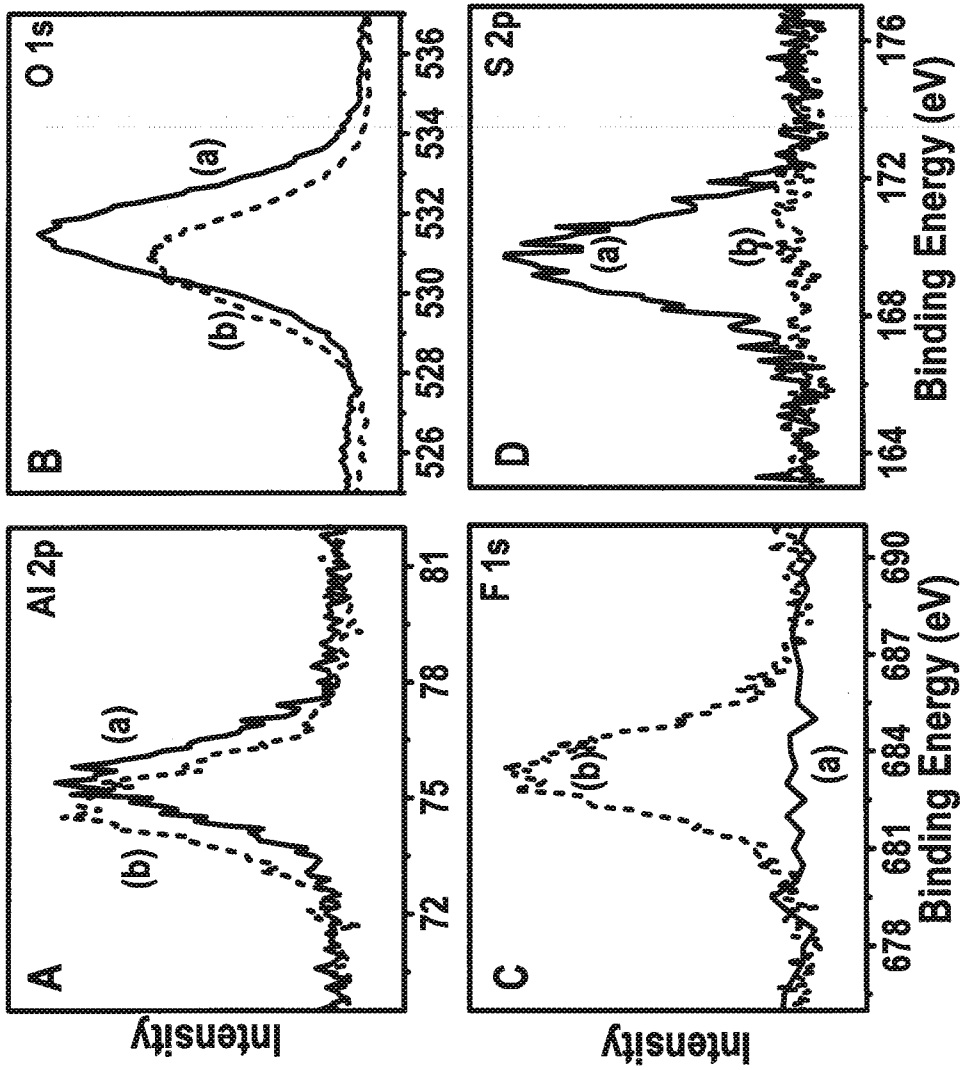


FIG. 5

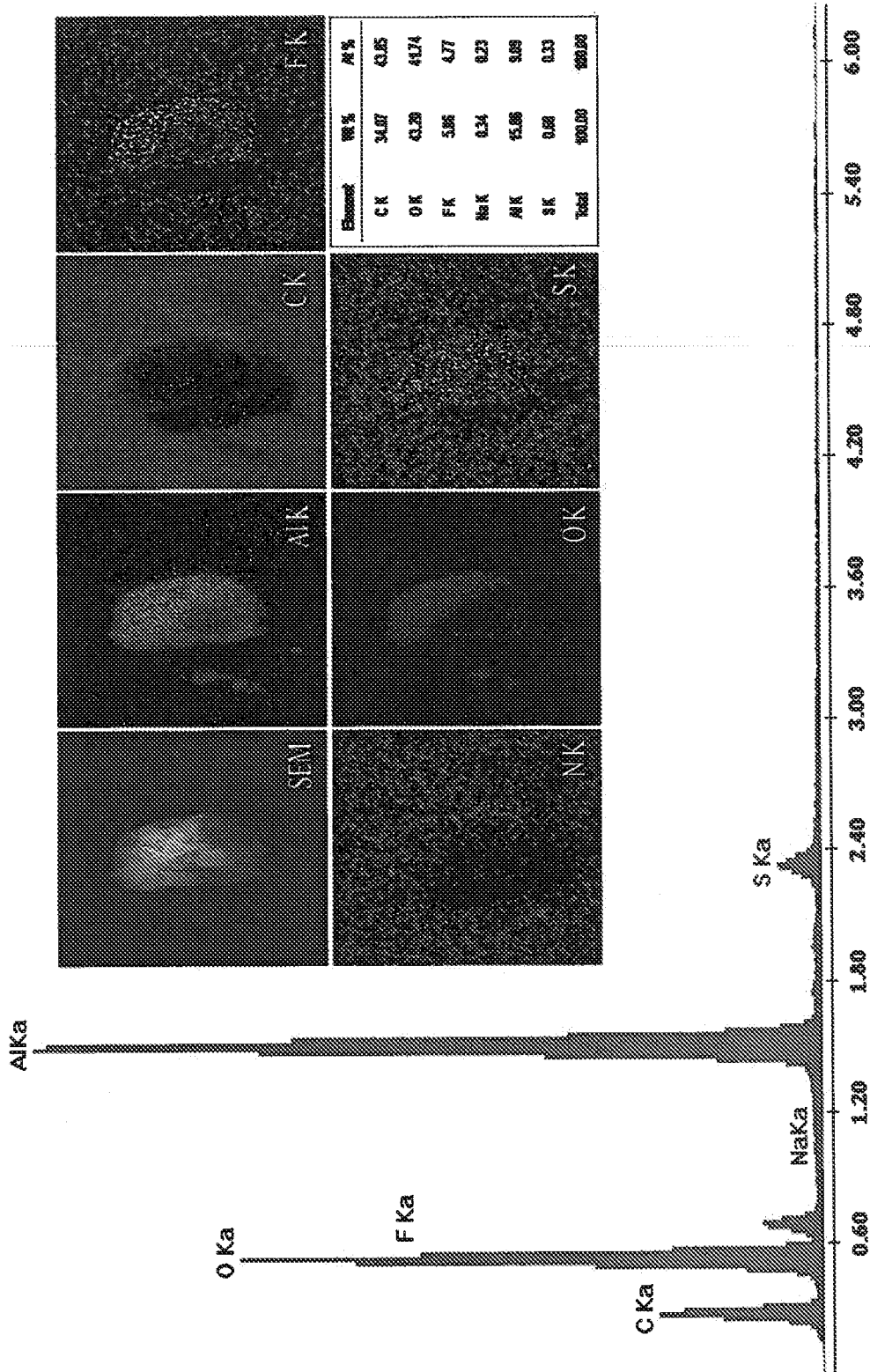


Figure 6

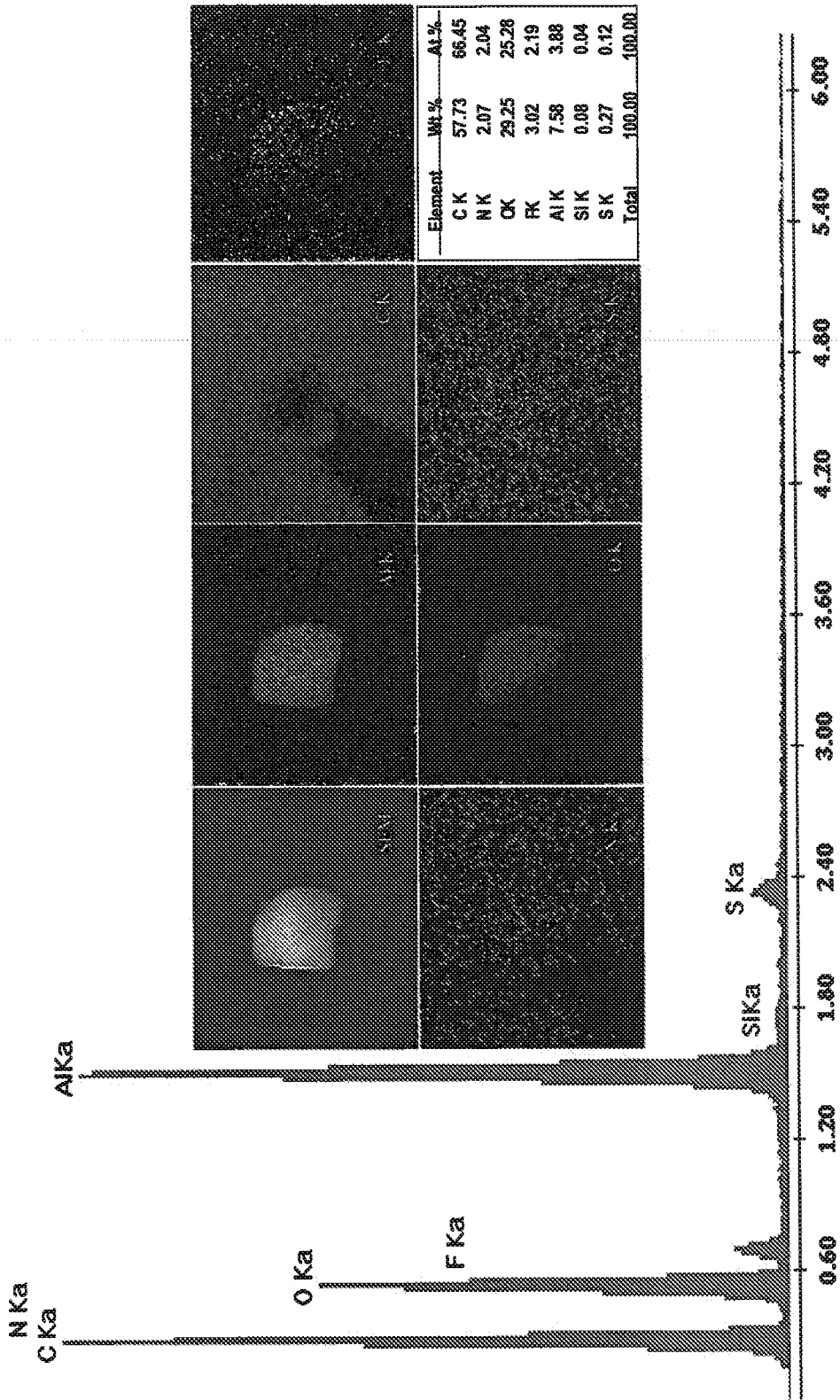


Figure 7

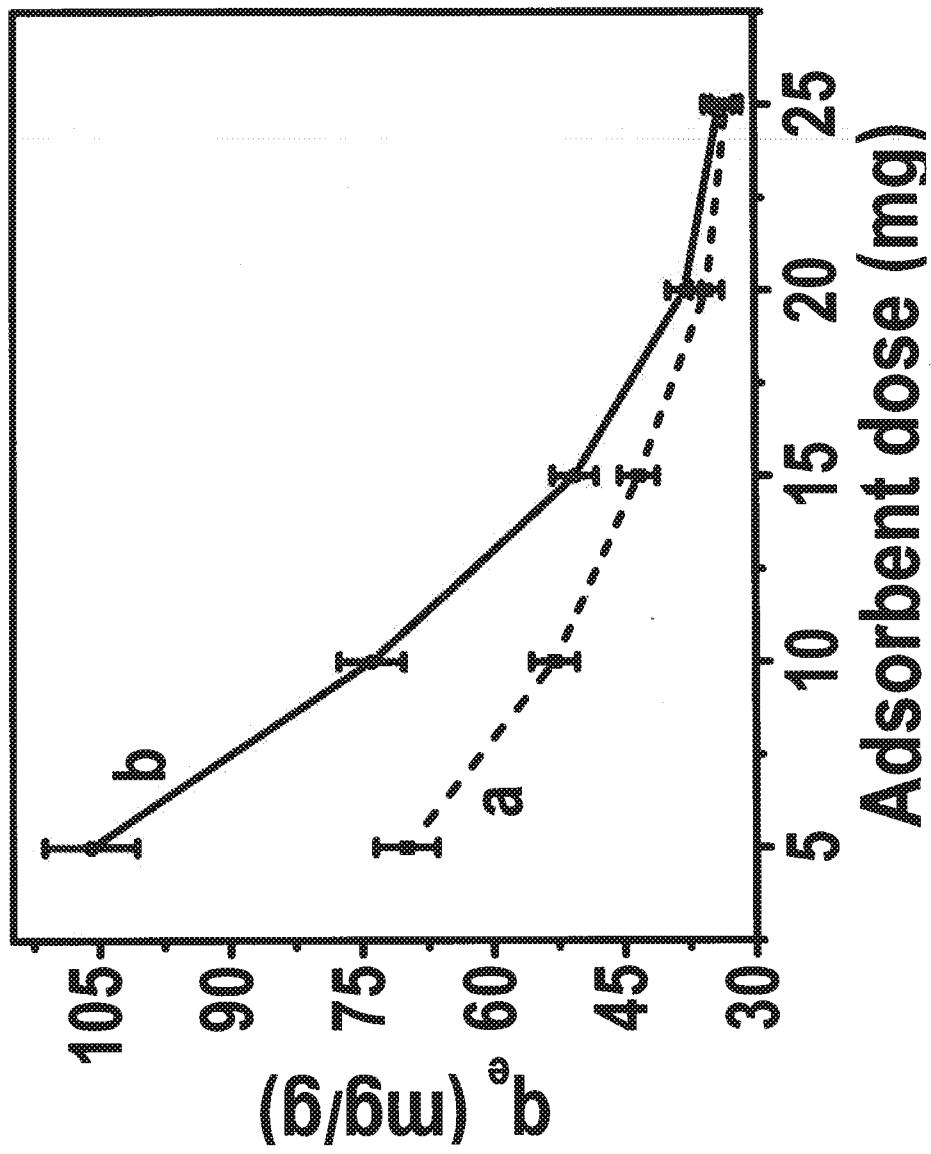


FIG. 8

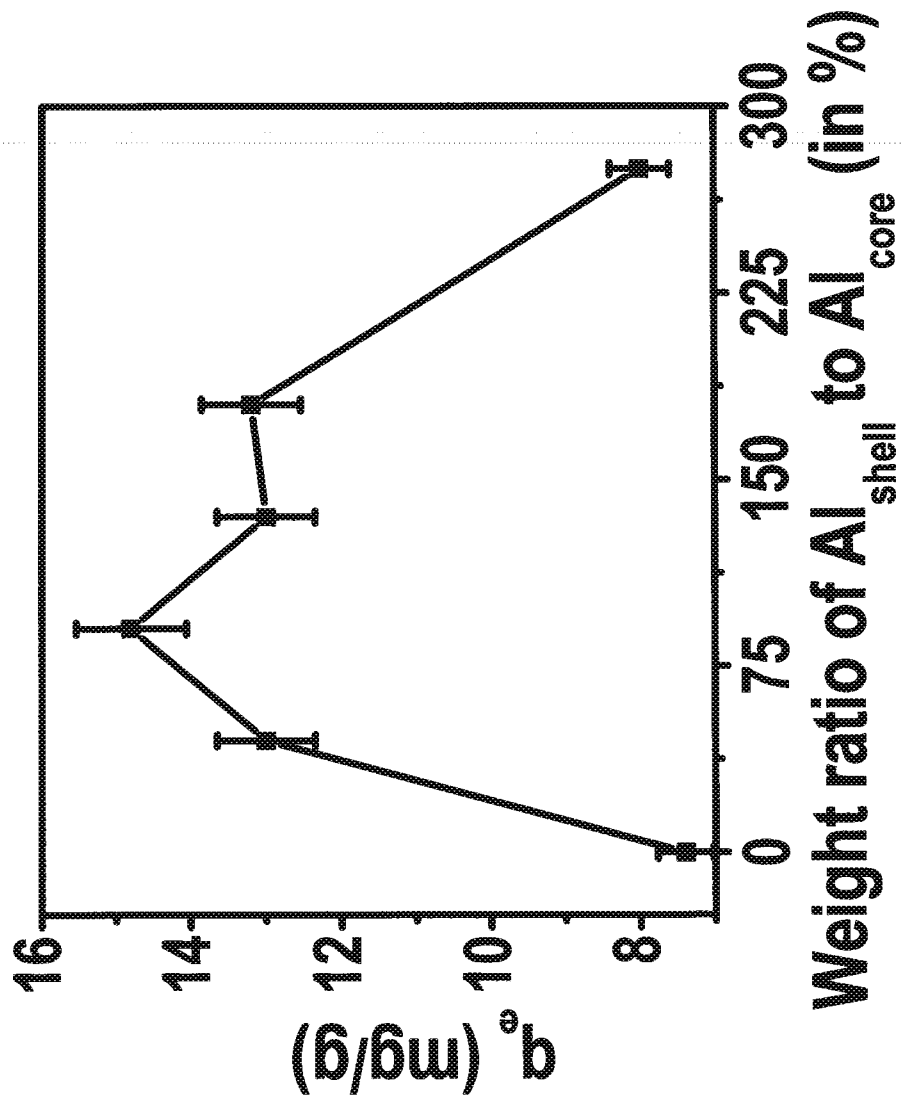


FIG. 9