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(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,

[Continued on next page]

(54) Title: METHOD FOR PRODUCTION OF NANOMATERIALS

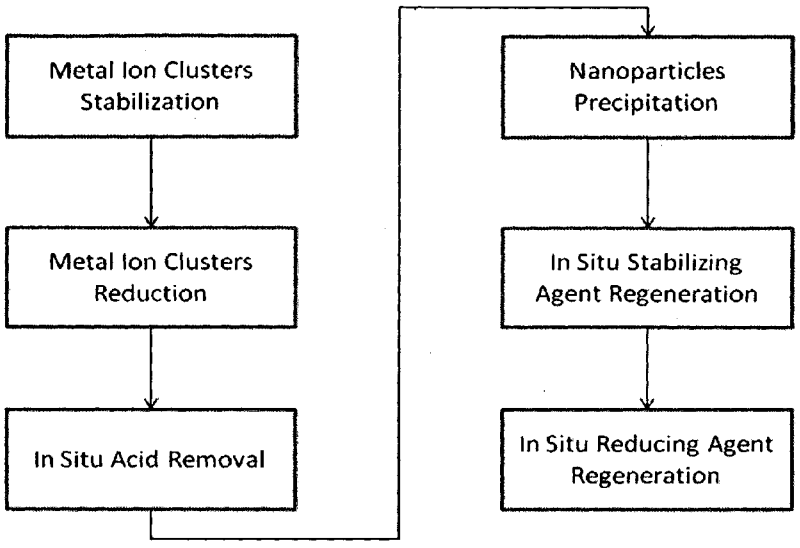

FIG 1

(57) Abstract: There is disclosed a method for sustainable production of nanomaterials using regenerative reagents, said method comprising the, steps of stabilizing metal ion clusters, reducing said metal ion clusters, providing in situ removal of acid using regenerative acid scavenger; regenerating stabilizer using catalytic hydrogenation; regenerating reducing agents using catalytic hydrogenation; and regenerating acid scavengers using alkaline washings.

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TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

METHOD FOR PRODUCTION OF NANOMATERIALS

FIELD OF THE INVENTION

Embodiments of the present invention are directed generally to a method for use in the production of nanomaterials, and more particularly to a method for the production of nanomaterials using regenerative stabilizer, reducing reagent and acid scavenger thus providing a solution to environmental concerns typically faced in nanomaterials production methods.

BACKGROUND OF THE INVENTION

In recent years, applications involving the use of nanomaterials have gained great momentum and much has been written about them. Applications involving the use of nanomaterials include, Electrochemical transducer, paste or ink for screen or inkjet printing, reference electrode, microelectrodes for amperometry, modified electrodes for catalytic oxidation of biomolecules and stripping voltammetry detection of trace levels of heavy metals.

In view of current advancements, nanotechnology research has contributed to novel material characteristics discovery that could further enhance current applications and even possibly generate new ones. One of the major interests and perhaps also a challenge to researchers in providing improved characteristics lies in the

methods of production of nanomaterials, particularly to ensure a highly reliable product outcome.

Currently in the production of nanomaterials, metal nanoparticles such as silver, gold and platinum nanoparticles are most commonly prepared by reduction of the respective metal ions with strong reducing agents such as sodium borohydride and hydrazine. Reduction with sodium borohydride gives boronates and boric acid as byproducts. It is widely known that these chemicals are hazardous to health and thus require special handling, meticulous preparative procedure and waste treatment. Likewise, hydrazine is very toxic and reactive and thus requires special care.

Furthermore, polymers containing nitrogen, oxygen and sulfur heteroatoms are often employed in nanoparticles preparations in order to stabilize the ionic metal clusters and the overcome the high surface energy in the newly formed nanoparticles. Highly water soluble poly saccharides, oligosaccharides, poly (vinyl pyrrolidone) or poly (vinyl alcohol) have been widely used to stabilize the electropositive intermediates in this process. Nevertheless, although these cations are expedient in stabilizing electropositive intermediates, they are not recovered in the process, discarded as waste and can pollute the environment.

In addition to the environmental concerns described in the above, in view of large scale production of nanoparticles, several products are required, such as, metal nanoparticles, metal oxide nanoparticles, and bulk metals. Therefore the reaction condition

must be controlled in order to increase yield and prevent formation of undesired products. Moreover, there are also concerns on the quality of the synthesized metal nanoparticles itself especially the range of size of the particles and the uniformity or regularity of its shape.

There exist various nanomaterials production methods gradually developed to accommodate the apparent shortcomings as discussed above. However many of the existing methods are costly and do not effectively solve the glaring disadvantages in producing nanomaterials outlined in the preceding paragraphs. An example of such methods is as disclosed in United States Patent No. US 20100034693, Li Yuning, et al. There is disclosed a process comprising: (a) preparing a reaction mixture comprising a silver salt, the reducing agent comprising a hydrazine compound, a thermally removable stabilizer, and an optional solvent, to form a plurality of silver-containing nanoparticles with molecules of the stabilizer on the surface of the silver-containing nanoparticles, wherein the reaction mixture generates an acid; and (b) removing the acid to produce the silver-containing nanoparticles substantially free of acid.

Recognizing the shortcomings of the existing nanomaterials production methods as discussed above, there is dire need to provide an improved method to be used in the production of nanomaterials which can effectively address the glaring environmental issues.

It is therefore a primary object of the present invention to provide a method for use in the production of nanomaterials, said method comprising the use of regenerative stabilizer, reducing reagent and acid scavenger.

It is yet an object of the present invention to provide a method for use in the production of nanomaterials, whereby the resulted encapsulated nanoparticles are prevented from forming lumps and help define the size of the synthesized particles.

It is yet a further object of the present invention to provide a method for use in the production of nanomaterials, whereby the stabilizer can be regenerated by reducing to alcohol by *in situ* and sustainable reduction process such as catalytic hydrogenation.

It is a another further object of the present invention to provide a method for use in the production of nanomaterials, whereby in this method, stabilized metal ion clusters are reduced by organic reducing agents that can be regenerated by sustainable reduction process such as catalytic hydrogenation.

It is yet a further object of the present invention to provide a method for use in the production of nanomaterials, whereby in this method, the accumulated acid in the reaction bath is continuously removed during the course of the reaction by imidazole acrylate polymer and the acid scavenger in one embodiment of the present invention can be regenerated by simple alkaline washings.

Still other embodiments of the present invention will become readily apparent to those skilled in the art from the following detailed description, wherein embodiments of the invention are described by way of illustration. As will be realized, the invention is capable of other and different embodiments and its several details are capable of modifications in various respects, all without departing from the spirit and the scope of the present invention.

SUMMARY OF THE INVENTION

In one aspect of the present invention there is provided a method for the production of nanomaterials comprising the steps of: providing or forming metal ion clusters stabilization; providing metal ion clusters reduction; removing acid using regenerative acid scavenger; regenerating stabilizer using catalytic hydrogenation; regenerating reducing agents using catalytic hydrogenation; and regenerating acid scavengers using alkaline washings.

BRIEF DESCRIPTION OF THE DRAWINGS

Features of the invention will be apparent from the following description when read with reference to the accompanying drawings:

FIG 1 shows the overall process flow of the method in accordance with a preferred embodiment of the present invention;

FIG 2 shows the stabilization metal ion clusters in a reduction process;

FIG 3 shows the process of regenerating a stabilizer by way of sustainable reduction process;

FIG 4 shows the process of regenerating reducing agent in accordance with the preferred embodiment of the present invention;

FIG 5 shows the process of removing acid in the reaction bath in accordance with the present invention;

FIG 6 shows the process of regenerating the acid scavenger can be regenerated by simple alkaline washings in accordance with the present invention;

FIG 7 shows the silvernano particles prepared in accordance with the method of the present invention.

FIG 8 shows the average size of nanoparticles prepared in accordance with the method of the present invention.

DETAILED DESCRIPTION

In the following description, reference is made to the accompanying drawings where, by way of illustration, specific embodiments of the invention are shown. It is to be understood that other embodiments

may be used as structural and other changes may be made without departing from the scope of the present invention. Also, the various embodiments and aspects from each of the various embodiments may be used in any suitable combinations. Accordingly, the drawings and detailed description are to be regarded as illustrative in nature and not as restrictive.

FIG 1 shows the overall view of the steps involved in accordance with the method of the present invention. In one embodiment, the method comprises the steps of providing or forming metal ion clusters stabilization, providing metal ion clusters reduction, removing acid using regenerative acid scavenger, regenerating stabilizer using catalytic hydrogenation, regenerating reducing agents using catalytic hydrogenation, and regenerating acid scavengers using alkaline washings.

It should be mentioned that the nanomaterials in accordance with the preferred embodiment of the present invention is at least one or combination of the following materials; silver, gold, platinum, nickel, bismuth, palladium.

According to the preferred embodiment of the present invention, the reaction takes place in a pressurized chamber, preferably slightly above atmospheric pressure i.e. 3 atm. In this condition, the oxidized reagents can be regenerated using *in* situ and sustainable reduction process such as catalytic hydrogenation

process. The acid scavenger can be regenerated by simple deprotonation process such as washing with alkaline solution.

As briefly discussed earlier, in order to obtain consistent size of silver nanoparticles which is the desirable feature in many nanomaterial based applications, the silver ions and particles need to be stabilized during the reduction process.

FIG 2 shows the stabilization metal ion clusters in a reduction process. During this process, clusters of metal ions and electropositive formed nanoparticles are stabilized by molecules and polymers having oxygen heteroatom groups assembled in a circular cage form. Further in accordance with the preferred embodiment of the present invention, the encapsulated nanoparticles are prevented from forming lumps and help define the size of the synthesized particles. The metal cation stabilizing molecule or polymer contains hydroxyl groups are oxidized to aldehyde or carboxylic acid during reduction of metal ion clusters.

FIG 3 shows the process of regenerating a stabilizer by way of sustainable reduction process, preferably catalytic hydrogenation. Accordingly, the stabilizer can be regenerated by reducing to alcohol by *in situ* and sustainable reduction process. It is preferred that stabilizer is at least one or combination of the following molecules; dextrin, gum arabic, cellulose, cellulose acetate, poly(vinyl alcohol), poly(vinyl pyrrolidone), starch, glycerol, menthol, terpineol, sorbitol, mannitol, xylitol, erythritol, sucrose, fructose, galactose.

FIG 4 shows the process of regenerating reducing agent in accordance with the preferred embodiment of the present invention. It is preferred that the stabilized metal ion clusters are reduced by organic reducing agents that are generated by sustainable reduction process, for instance, but not limiting to, catalytic hydrogenation. In this process, strong and regenerative organic reducing agents can be used, such as, but not limiting to, hydroquinone, anthraquinone, napthaquinone, uric acid, ascorbic acid and citric acid that can reduce metal ion at mild conditions, and can be regenerated by catalytic hydrogenation are preferred.

Further, it is preferred that the reducing agent is at least one or combination of the following chemicals ;sodium citrate, calcium citrate, trisodium citrate, tripotassium citrate, citric acid, hydrogen citrate, dihydrogen citrate, potassium citrate, ascorbic acid, glucose, uric acid, oxalic acid, disodium oxalate, calcium oxalate, formic acid, hydroquinone, anthraquinone, 2-ethyl-9,10-anthraquinone, menadione, parietin, napthaquinone.

According to the preferred embodiment of the present invention, the hydrogenation catalyst is at least one or combination of the following materials; palladium, ruthenium, zinc, copper, nickel.

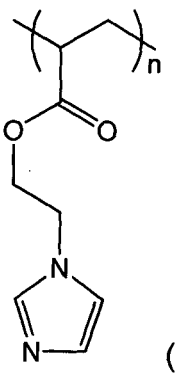
It is known that formation of silver nanoparticles dispersion can be visually inspected by formation of brown, yellowish or greenish

colloids, depending on the size of the nanoparticles, a few minutes after addition of the regenerative reducing agent. The nanoparticles can be induced to precipitate out from the homogenous colloid solution using centrifuge.

Further in accordance with the preferred embodiment of the present invention, the metal ion cluster stabilizing agents and reducing agents can be reduced *in situ* while the nanoparticles are being formed. In this option there is a possibility that the reduction process participates in reducing metal ion clusters. This can however provide positive effect of reducing the formation of silver oxide nanoparticles and thus resulting to increasing the rate of nanoparticles formation.

FIG 5 shows the process of removing acid in the reaction bath in accordance with the present invention. The accumulated acid in the reaction bath is continuously removed during the course of the reaction by imidazole acrylate polymer.

FIG 6 shows the process of regenerating the acid scavenger can be regenerated by simple alkaline washings in accordance with the present invention. It is preferred that the regenerative acid scavenger has having the following structure (Structure 1):



(Structure 1)

With this method described in accordance with the preferred embodiments of the present invention, the resulting nanomaterial can be measured and deduced into the average particle size and range of samples using standard apparatus such as Scanning Electron Microscope (SEM) and Small Angle X-ray Scattering (SAXS).

Examples below provide further elucidation of the method in accordance with the present invention, whereby it should be understood that these examples should not be taken as restrictions to the intended scope of protection which will be defined in the claims.

EXAMPLE 1

Preparation of Silver Nanoparticles

Beads of palladium-carbon catalyst and imidazole acrylate polymeric acid scavenger were placed at the bottom of a pressurizable chamber. Poly (vinyl alcohol) (1.0g) were added into and 40mL of deionized

water was added into the pressurizable reaction vessel. The homogenous solution was magnetically stirred at room temperature for 30 minutes when all the solid materials were completely dissolved. Silver nitrate (0.5g, 0.002 mole) in 10mL of deionized water was added drop-wise into the reaction mixture with gentle stirring. 2-Ethyl-9,10-dihydroanthraquinone (0.005 mole) in ethanol was added drop-wise into the reaction mixture. The reaction mixture was stirred for additional 30 minutes at room temperature. The homogenous colloid was decanted and centrifuged to induce precipitation. The size distribution of the silver nanoparticles was examined using SEM and SAXS. The average size of approximately 70 nm has been assigned to the silver nanoparticles based on these methods. The silver nanoparticles obtained based on the above method is shown in FIG 7, and the average size of silver nanoparticles prepared is shown in FIG 8.

EXAMPLE 2

Regeneration of Stabilizer and Reducing Agents

During nanoparticles formation alcohol groups in poly (vinyl alcohol) metal ion cluster stabilizing agent were oxidized to aldehyde and carboxylic acid. Similarly the reducing agent 2-ethyl-9,10-dihydroanthraquinone was oxidized to 2-ethyl-9,10-anthraquinone. These reagents were regenerated by pressurizing the reaction chamber with hydrogen gas until the pressure reached 3 atm.

With all valves tightly closed, the used reaction bath was stirred under pressurized condition at room temperature for 2 hours. The reagent was successfully regenerated when the dark color of the solution faded away to afford almost clear solution.

EXAMPLE 3

Regeneration of Imidazole Acid Scavenger

The beads of used imidazole acrylate acid scavenger were removed from the reaction chamber and washed three times with saturated sodium bicarbonate solution. Then the beads were placed in three-neck round-bottom flask and 0.1M solution of potassium hydroxide was added and the solution stirred for 1 hour. The beads were finally washed with brine solution and deionized water, dried in the oven and stored in a desiccator before use.

While the invention has been particularly shown and described with reference to the illustrated embodiments, those skilled in the art will understand that changes in form and detail may be made without departing from the scope of the invention.

CLAIMS

1. A method for the production of nanomaterials comprising the steps of:

providing or forming metal ion clusters stabilization;

providing metal ion clusters reduction;

removing acid using regenerative acid scavenger;

regenerating stabilizer using catalytic hydrogenation;

regenerating reducing agents using catalytic hydrogenation; and

regenerating acid scavengers using alkaline washings.

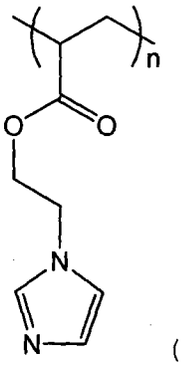
2. The method as claimed in Claim 1 wherein the nanoparticles is at least one or a combination of the following materials; silver, gold, platinum, nickel, bismuth, palladium.

3. The method as claimed in Claim 1 wherein the stabilizer is at least one or a combination of the following molecules; dextrin, gum arabic, cellulose, cellulose acetate, poly(vinyl alcohol), poly(vinyl pyrrolidone), starch, glycerol, menthol, terpineol, sorbitol, mannitol, xylitol, erythritol, sucrose, fructose, galactose.

4. The method as claimed in Claim 1 wherein the reducing agent is at least one or combination of the following chemicals ;sodium citrate, calcium citrate, trisodium citrate, tripotassium citrate, citric acid, hydrogen citrate,

dihydrogen citrate, potassium citrate, ascorbic acid, glucose, uric acid, oxalic acid, disodium oxalate, calcium oxalate, formic acid, hydroquinone, anthraquinone, 2-ethyl-9,10-anthraquinone, menadione, parietin, napthaquinone.

5. The method as claimed in Claim 1 wherein the regenerative acid scavenger has the following structure (Structure 1):



(Structure 1)

6. The method as claimed in Claim 1 wherein the hydrogenation catalyst is at least one or combination of the following materials; palladium, ruthenium, zinc, copper, nickel.

7. The method as claimed in Claim 1 wherein the steps are carried out in a pressurized chamber, preferably slightly above atmospheric pressure, 3 atm.

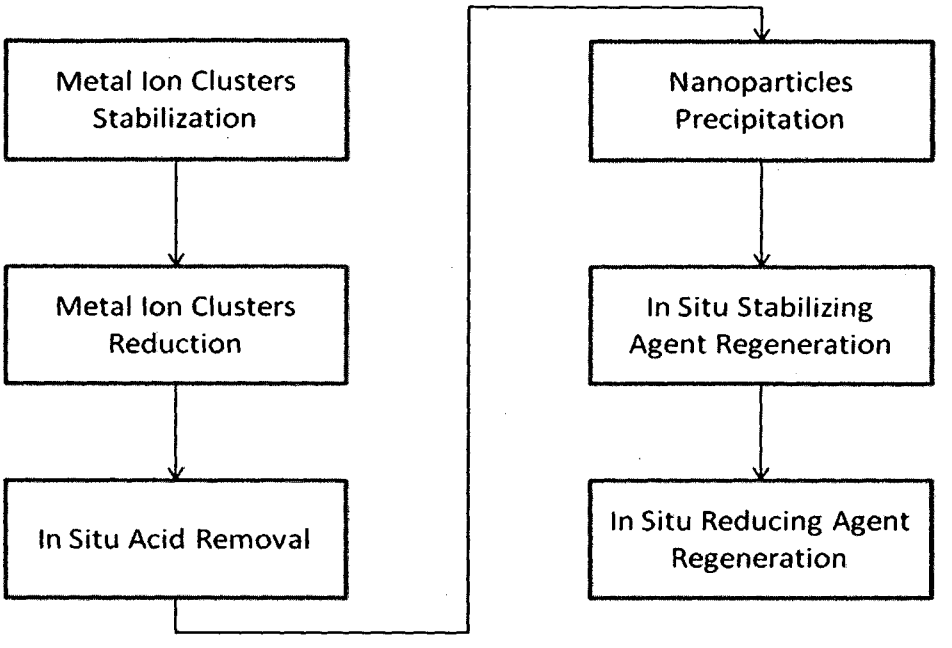

Metal Ion Clusters Stabilization
Metal Ion Clusters Reduction
In Situ Acid Removal
Nanoparticles Precipitation
In Situ Stabilizing Agent Regeneration
In Situ Reducing Agent Regeneration

FIG 1

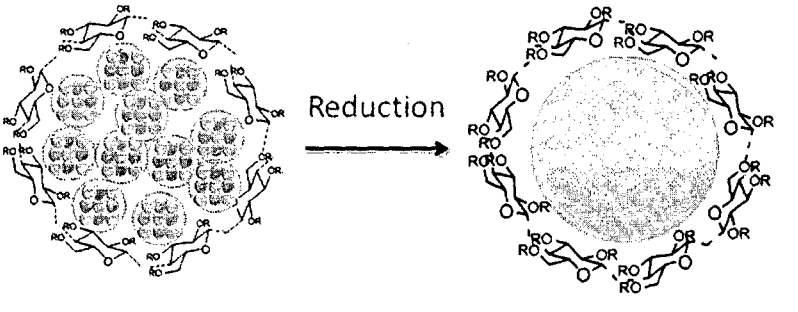

Reduction
Stabilized Metal Ion Clusters
Stabilized Nanoparticle

FIG 2

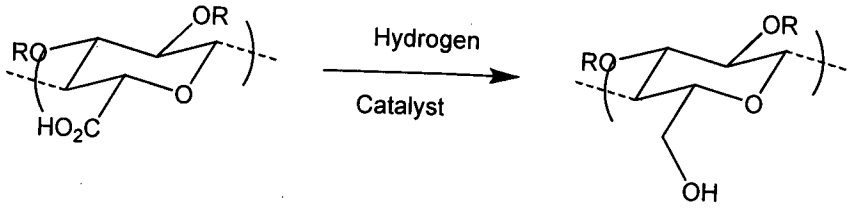

OR
RO
O
HO_2C
Hydrogen
Catalyst
OR
RO
O
OH

FIG 3

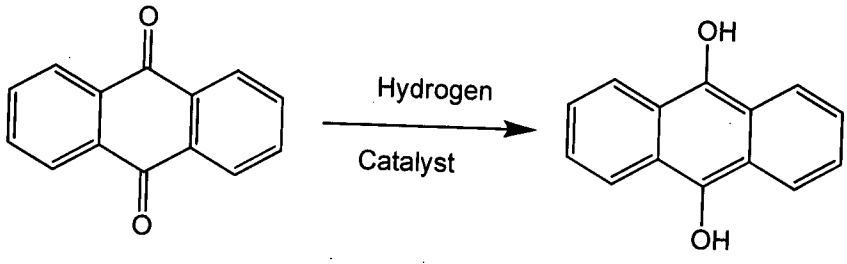

O
O
Hydrogen
Catalyst
OH
OH

FIG 4

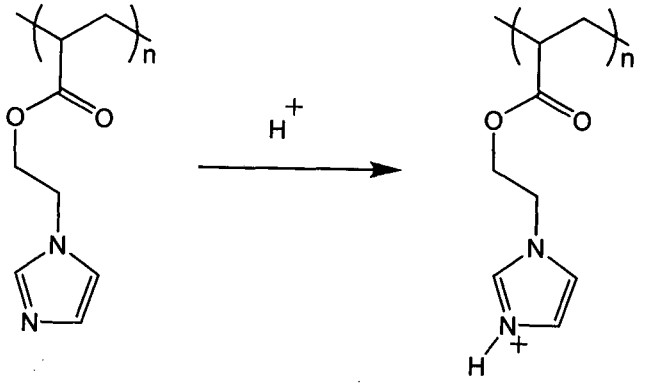


FIG 5

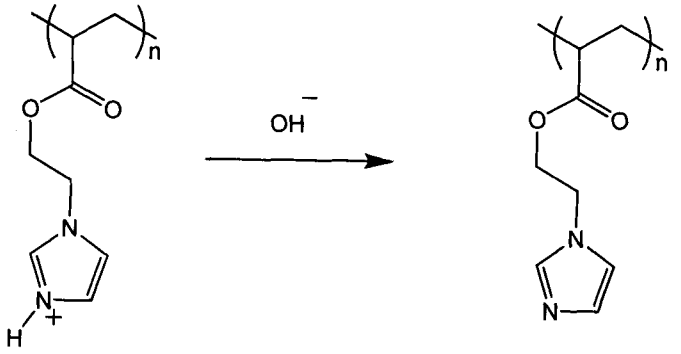


FIG 6

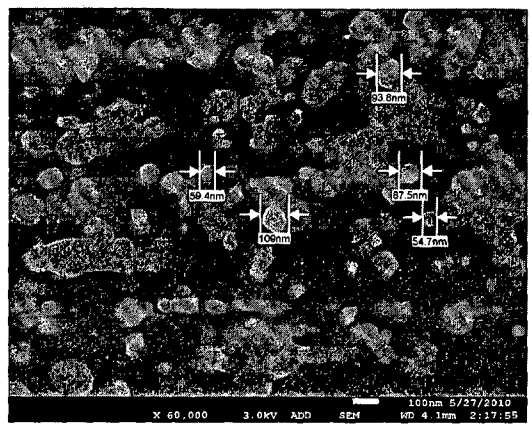

93.8nm
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FIG 7

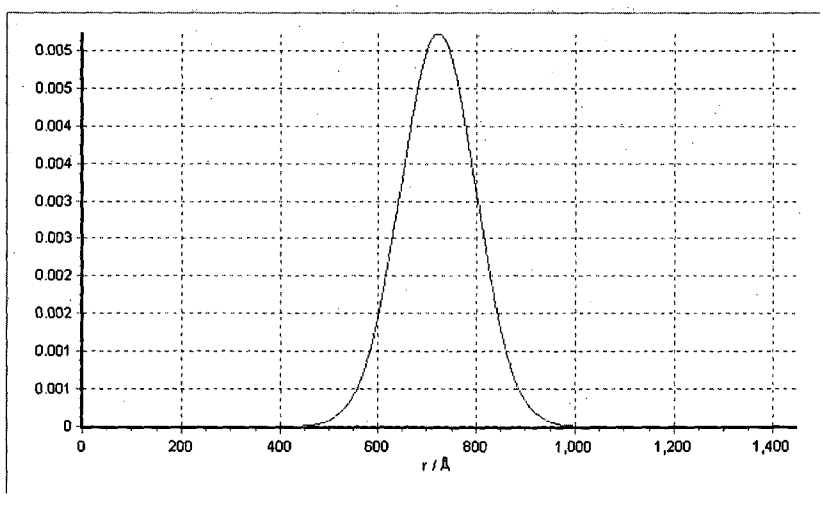
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FIG 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/MY2012/000127

A. CLASSIFICATION OF SUBJECT MATTER
INV. B22F9/24
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)
B22F

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, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2010/034693 A1 (LI YUNING [CA]) 11 February 2010 (2010-02-11) cited in the application the whole document -----	1-7
A	US 2010/189901 A1 (CHUNG KWANG-CHOON [KR] ET AL) 29 July 2010 (2010-07-29) -----	1-7
A	RIVAS B L ET AL: "Resins with the ability to bind copper and uranyl ions", 5 February 2006 (2006-02-05), JOURNAL OF APPLIED POLYMER SCIENCE 20060205 JOHN WILEY AND SONS INC. US, VOL. 99, NR. 3, PAGE(S) 706 - 711, XP002686914, -----	1-7

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 November 2012	22/11/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Morra, Valentina

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/MY2012/000127

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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