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(71) Applicant: **THE UNIVERSITY OF QUEENSLAND** [AU/AU]; C/- Cullens Patent and Trademark Attorneys, Level 32, 239 George Street, Brisbane, Queensland 4000 (AU).

(72) Inventors: **YU, Chengzhang**; C/- Cullens Patent and Trademark Attorneys, Level 32, 329 George Street, Brisbane, Queensland 4000 (AU). **ZHOU, Liang**; C/- Cullens Patent and Trademark Attorneys, Level 32, 329 George Street, Brisbane, Queensland 4000 (AU).

(74) Agent: **CULLENS PATENT AND TRADEMARK ATTORNEYS**; Level 32, 329 George Street, Brisbane, Queensland 4000 (AU).

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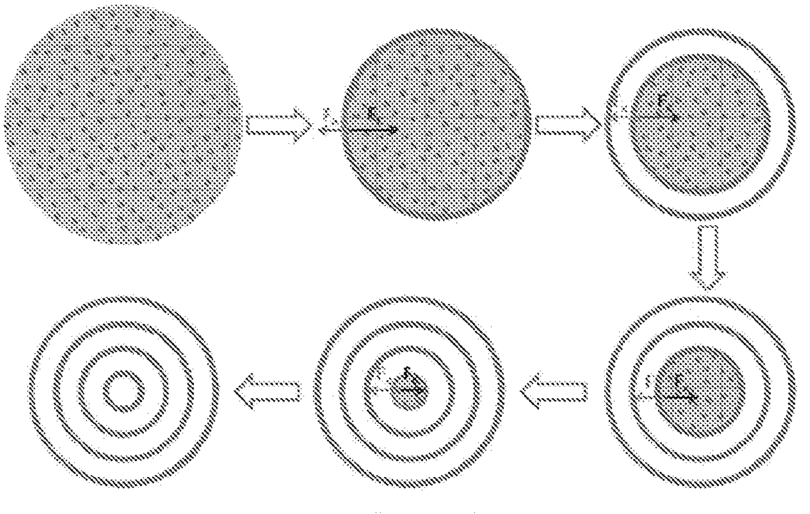

Figure 1

(57) Abstract: A method for forming multi-shelled hollow structures comprising metal oxide, the method comprising the steps of: forming a solution containing at least one dissolved metal compound and at least one organic compound, spray drying the solution to form composite particles containing at least one metal species and organic material, and heating the composite particles by increasing temperature at a predetermined rate to form the multi-shelled hollow structures comprising metal oxide.

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TITLE

Method for producing hollow structures

TECHNICAL FIELD

[0001] The present invention relates to a method for making hollow structures, such as hollow particles or spheres. More specifically, the present invention relates to a method for forming hollow structures having a plurality of shells. The hollow structures may be used in a lithium ion battery anode or to remove contaminants, such as heavy metals and polyanions, from solution.

BACKGROUND ART

[0002] Hollow structures, a unique family of materials with low density and high surface area versus conventional materials, and shell permeability, have attracted tremendous attentions in drug delivery, gas sensors, adsorption, as well as energy storage and conversion. Recently, efforts have been dedicated to the rational design of complex multi-shelled hollow structures due to both their aesthetic beauty and the opportunity for further physical chemical properties tailoring by manipulating the shell structure. The most popular approach for the fabrication of multi-shelled hollow structures involves the shell-by-shell deposition of desired materials onto sacrificial templates followed by selective template removal. Hard templates, such as monodispersed polymer, silica, carbon, and metal/metal oxide nanoparticles, or soft ones, such as micelles, have been widely utilized as the sacrificial templates. However, the templating approach is usually tedious and costly; and the more complex the target structure, the more complicated the synthesis procedure. Therefore, it is highly desirable to develop a simple and scalable method for the fabrication of MSHSs.

[0003] Hematite (α-Fe_2O_3), the most stable form of iron oxide, has been extensively studied as water splitting photoanodes, media for the absorptive removal of arsenic and phosphate and heavy metal species from water, gas sensors, and active anode materials for lithium ion batteries (LIBs). Lithium ion battery technology is facing ever increasing challenges in its traditional applications in consumer electronics where the power demands of portable electronic equipment are increasing at a greater rate than improvements in charge storage capacity of the batteries powering them, leading to shorter run times between charges. It is widely recognised that there is no feasible alternative to lithium ion batteries for powering portable electronic equipment in the short to medium term. Efforts to increase the charge storage capacity of lithium ion batteries have largely focussed on the development of anode materials with inherently large lithium storage capabilities, in particular, silicon, tin, aluminium, antimony, tin oxide and lithium metal. In the case of silicon for example, practical charge storage capacity is approximately 3600 mAh/g compared with 372 mAh/g for conventional graphite anode material. Despite the large charge storage capacities of these materials, their practical implementation has been hampered by poor cycle life that results from the significant expansion and subsequent contraction in the volume of the active material that occurs on lithium insertion and extraction processes respectively as the battery is cycled. Hematite offers a charge storage capacity of 1007 mAh/g, can be fabricated from abundant raw materials, is low cost and is environmentally benign. Despite these advantages, the application of α-Fe_2O_3 in LIBs is still hampered by the same large volume variations during Li^+ insertion/extraction (~ 96 %) that afflict other high capacity anode materials, which causes the notorious problem of pulverization and the subsequent capacity fading. To alleviate the volume change issue in anode materials, several strategies have been proposed. One effective strategy is designing unique nanostructures, such as hollow structures and porous materials. The idea is to utilize the free space in the nanostructured electrode material to partially accommodate the drastic volume change. However, the creation of free space in a material also reduces the tap density of the material which in a lithium ion battery translates into a lower volumetric charge storage capacity. As such, the introduction of free space to improve cycle life must be balanced against the original desire to maintain charge storage capacity. Another commonly used approach is fabricating nanocomposites of carbon and α-Fe_2O_3, where the carbon acts as a buffering layer. However, the synthesis of state-of-the-art α-Fe_2O_3 based nanostructures and nanocomposites usually involves expensive sacrificial templates, cumbersome multisteps, or time-consuming hydrothermal/solvothermal reactions in autoclaves. This situation inspires us to search for simple, economic, and scalable ways to produce α-Fe_2O_3 anode materials with satisfactory specific capacity and rate capability.

[0004] In the field of water treatment, iron oxides are well known as materials that adsorb polyanion contaminants from water including arsenic (III) and arsenic (V) species, phosphate anions and some heavy metals including lead, cadmium and chromium. In the case of arsenic removal, hematite works by adsorbing multilayers of arsenic species on the surface of the material. As such, strategies to improve the performance of adsorbent materials have focussed on increasing surface area and leading commercial materials typically have surface areas in the range 200-300 m^2/g.

[0005] Chromium based oxides and vanadium based oxides, either binary or ternary oxides, have proven to be very effective catalysts for oxidative dehydrogenation of ethane to ethylene. The catalytic conversion of alkanes into their corresponding alkenes by the oxidative or nonoxidative dehydrogenation are of increasing importance because of growing demand for alkenes. Ethane is the second major component of natural gas. Thermal cracking of hydrocarbons, such as ethane, in the presence of steam is currently the main source of ethylene. However, steam cracking of ethane to ethylene is a highly endothermic process, which must be performed at high temperatures and consumes a great deal of energy. Moreover, high temperature may result in other undesirable reactions producing coke, the existence of which deteriorates the catalytic activity and reactor performance. Oxidative dehydrogenation of ethane by oxygen or carbon dioxide has been proposed as an alternative route to the process of thermal cracking of ethane. It is an exothermic process and can be performed at lower temperatures. The low temperature operation and exothermic reactions can significantly reduce the external heat input and lessen the coke formation.

[0006] Spray drying is a widely applied technology in chemical, pharmaceutical, and food industry. It enables simple, continuous, and scalable production of fine particles. Spray drying involves forming a solution or slurry and spraying the solution or slurry through a hot gas to dry the solution or slurry and to form fine particles of material.

[0007] It will be clearly understood that, if a prior art publication is referred to herein, this reference does not constitute an admission that the publication forms part of the common general knowledge in the art in Australia or in any other country.

SUMMARY OF INVENTION

[0008] The present invention is directed to a method for forming hollow structures, which may at least partially overcome at least one of the abovementioned disadvantages or provide the consumer with a useful or commercial choice.

[0009] In a first aspect, the present invention provides a method for forming multi-shelled or yolk-shell hollow structures comprising metal oxide, the method comprising the steps of:

- forming a solution containing at least one dissolved metal compound and at least one organic compound,
- spray drying the solution to form composite particles containing at least one metal species and organic material, and
- heating the composite particles by increasing temperature at a predetermined rate to form the multi-shelled or yolk-shell hollow structures comprising metal oxide.

[0010] In one embodiment, the solution is formed by dissolving a metal compound and at least one organic compound in water.

[0011] In some embodiments, the at least one dissolved metal compound is formed by dissolving a metal-containing compound in a solvent. The solvent is preferably water.

[0012] The at least one dissolved metal compound may comprise a metal nitrate, a metal chloride, or a metal sulphate. Other metal compounds that are soluble may also be used. Although inorganic metal compounds are preferred, in some instances, organic metal compounds may be used, such as a metal acetate, a metal alkoxide, a metal citrate, a metal lactate, a metal gluconate (such as a metal D-gluconate), or a metal oxalate. It will be appreciated that this list is not exhaustive and the other metal compounds may be used. An ammonium-metal compound may be used.

[0013] The at least one dissolved metal compound suitably includes iron. In another embodiment, the at least one dissolved metal compound suitably includes zinc, tin, vanadium, manganese, titanium, chromium, nickel, cobalt, aluminium or mixtures of two or more thereof, such as mixtures of nickel/manganese, or nickel/cobalt/manganese, or nickel/cobalt/aluminium..

[0014] The method of the present invention may be used to form hollow structures of Fe_2O_3, TiO_2, SnO_2, MnO_x, $FeMnO_x$, Cr_2O_3, vanadium oxide, etc.

[0015] The at least one dissolved metal compound may comprise two or more dissolved metal compounds. The two or more dissolved metal compounds may comprise an iron compound and another metal compound.

[0016] In some embodiments, the at least one organic compound comprises an organic compound that dissolves in water. The at least one organic compound may comprise an organic compound that can be removed by calcination.

[0017] Without wishing to be bound by theory, the present inventors have postulated that the organic compound acts as an organic matrix in the composite particles formed by the spraydrying step. The organic matrix assists in confining the salt and binding the composite particle, forming a homogenous mixture after spray drying and allowing for fine control over the nanostructures during calcination. It also acts to lower the hygroscopicity of the spray dried composite particles.

[0018] The organic material may comprise sucrose, glucose, oxalic acid, polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene glycol and citric acid. Other organic materials may be used.

[0019] The molar ratio of organic compound to dissolved metal in the solution may vary depending upon the metal compound(s) and organic material being used. For example, if iron nitrate and sucrose are being used as starting materials, the molar ratio of organic compound to dissolved metal in the solution may vary from 5/10 to 15/10, more preferably from 7.5/10 to 10/10. However, using other metal compounds, or using other organic materials may result in quite different molar ratios of organic compound to dissolved metal being used to form the multi-shelled hollow structures. For example, a glucose/iron nitrate ratio of 20/10 can lead to multilayered Fe_2O_3, an oxalic acid/ammonium metavanadate ratio of 30/10 can lead to yolk-shell structured V_2O_5. The skill person would really appreciate that quite simple experimental work will be able to ascertain a range of suitable ratios of organic compound to dissolved metal in the solution for the particular starting materials being used.

[0020] In some embodiments, the as-synthesized composite particles will typically comprise solid particles. The particle size of the composite particles is largely determined by the size of the nozzle in the spray drier, the flow rate of solution to the nozzle and the dry conditions in the spray drier. Persons skilled in the art will appreciate that particles of a desired size may be formed across a relatively wide range of particle sizes using spray drying techniques.

[0021] In other embodiments, the as-synthesized composite particles may comprise hollow particles or collapsed hollow particles. The present inventors believe that the form of the as-synthesised composite particles is somewhat dependent upon the organic material that is being used.

[0022] In some embodiments, the temperature of the composite particles is increased at a predetermined rate by increasing the temperature at a constant rate, such as by increasing the temperature at a constant rate of between 0.5°C per minute and 10°C per minute (for example, 0.5 °C/min, 2 °C/min, 5 °C/min and 10 °C/min).

[0023] In other embodiments, the temperature is increased at a predetermined rate by increasing the temperature at a non-constant rate or a non-linear rate.

[0024] In some embodiments, the composite particles are removed from the spray drier or are recovered from the spray drier prior to the heating step.

[0025] In some embodiments, the composite particles are heated by placing the composite particles in a furnace and increasing the temperature of the furnace at a predetermined rate.

[0026] In some embodiments, the furnace is at room temperature (~25°C) at the commencement of the heating step. The heating step is desirably conducted until the temperature is increased to or above a minimum temperature at which the organic material is removed from the particles and the desired metal oxide phase or phases have been formed. For example, in preparing haematite hollow structures from an initial composition containing sucrose and iron nitrate, the thermogravimetric analyser (TGA) curve shows that the burn off of sucrose and decomposition of iron nitrate is complete at 400°C. Therefore, in using this combination of starting materials, there is little benefit in extending the heating step above a temperature of 400°C. However, higher calcination temperatures (for example up to 600°C) were tried and the desired hollow microstructures were obtained. The skilled person will appreciate that the minimum temperature to which the composite particles must be heated will be very in accordance with the starting materials utilised.

[0027] In some embodiments, the multi-shelled hollow structures formed in the present invention may be maintained at a high temperature for a period of time in order to improve the crystallinity of those structures.

[0028] The multi-shelled hollow structures may comprise multi-shelled hollow particles or multi-shelled hollow spheres.

[0029] In some embodiments, the multi-shelled hollow structures comprise three or more shells wherein shells of decreasing size are located within larger shells. Suitably, the multi-shelled hollow structures comprise at least four shells, or suitably comprise four shells.

[0030] In desirable embodiments of the present invention, all of the shells comprise hollow shells. The multi-shelled hollow structures suitably do not have a solid core.

[0031] In some embodiments, the yolk-shell hollow structures may comprise yolk-shell hollow spheres or yolk-shell hollow particles. In other embodiments, the core particles (i.e., the yolk) may be solid.

[0032] The metal oxide that forms the multi-shelled hollow structures may comprise hematite (Fe_2O_3). The metal oxide that forms the multi-shelled hollow structures may comprise a complex metal oxide or a mixed metal oxide containing two or more metals in the oxide structure. The two or more metals may comprise iron and one or more other metals.

[0033] The multi-shelled hollow structures may comprise particles having a size falling within the range of 200 to 4000nm, or within the range of 400 to 2000 nm.

[0034] In some embodiments, the multi-shelled hollow structures may comprise a plurality of particles joined to other particles to form an aggregate. The plurality of particles may be formed into an aggregate by necking at regions where one particle comes into contact with an adjacent particle. At these regions, "bridges" may be formed between the particles to thereby hold the particles together in a fused aggregate of particles such that the size of the aggregates is larger than that of the primary particle building blocks. In water treatment applications, small particles often wash through the filter housing containing the particles, causing discolouration of the filtered water, loss of contaminant adsorption capacity in the filter and the loss of contaminant-containing particles into the treated water stream. The use of larger particles can prevent this loss of material. Small particles also pack more densely than larger particles providing smaller interparticles dimensions for water to flow through. This has the effect of decreasing the flow rate of water through media compared to media composed of larger particles where interparticle void spaces are larger. Lower flow rates in turn limit the productivity of water treatment systems and makes blockage of filter systems more likely to occur. In contrast, fused aggregates with their larger particle size have the advantages of allowing higher flow rates to be achieved with a lower probability of blocking.

[0035] In another aspect, the invention resides broadly in a method for forming aggregate particles ("fused aggregates") from multi-shelled hollow structures, the method comprising the steps of mixing the multi-shelled hollow structures with a chemical species that is a metal hydroxide or is capable of forming a metal hydroxide to form a mixture, and processing the mixture to produce the aggregate particles.

[0036] Any suitable metal hydroxide may be used, such as, but not limited to, copper hydroxide, titanium hydroxide, aluminium hydroxide, iron hydroxide, nickel hydroxide or the like, or a combination thereof. The metal hydroxide may be provided in any suitable form, such as, but not limited to a solid, solution or gel. More preferably, however, the metal hydroxide is in the form of a gel. Preferably, the metal hydroxide gel comprises aluminium hydroxide gel. Preferably, the metal hydroxide gel is a wet metal hydroxide gel.

[0037] In place of the metal hydroxide, fused aggregates may be formed by mixing the multi-shelled hollow structures with a chemical agent that is a precursor to metal hydroxides. In this case, the chemical agent precursor precipitates to form a metal hydroxide that cements the multi-shelled hollow structures together. The formation of metal hydroxides from metal-based precursors via reactions such as hydrolysis and precipitation are well known to those in the art. For example, a titanium hydroxide species could be formed using a precursor such as titanium isopropoxide or titanium trichloride which undergo hydrolysis to form the titanium hydroxide product.

[0038] The multi-shelled hollow structures and the metal hydroxide gel may be mixed using any suitable technique. Preferably, however, the mixing of the multi-shelled hollow structures and the metal hydroxide gel is achieved using mechanical mixing. A skilled addressee will understand that the exact nature of the mechanical mixer used to achieve the mixing is not critical.

[0039] It is envisaged that the mixing of the multi-shelled hollow structures and the metal hydroxide gel will result in the formation of a mixture. Once mixing is complete, the mixture may be processed to form the aggregate particles. The mixture may be processed using any suitable technique, such as extruding the mixture through a screen, sieve, mould or the like, or any suitable combination thereof. The choice of processing method used will depend on the desired particle size of the final fused aggregates. Most preferably, the mixture may be extruded through a screen or sieve. The size of the apertures in the screen or the sieve is not critical, and a skilled addressee will understand that the size of the apertures in the screen or sieve through which the mixture is extruded will be dependent on the desired size of the aggregate particles.

[0040] Once extruded, the aggregate particles may be dried and/or calcined. Following drying and/or calcination, the fused aggregates may be further processed to refine the particle size. By providing control of the particle size in this step, less precise processing of the mixture prior to drying/calcination to control particle size is required. Methods for achieving particle size control in this manner include, but are not limited to, milling techniques such as ball milling, crushing, particle size reduction using high shear forces, high pressure homogenisation and other techniques known to those skilled in the art.

[0041] In lithium ion battery applications electrodes typically contain a number of components including the active, charge storage material, a particle additive to promote electronic conductivity such as carbon black or acetylene black and a polymeric binder that acts to hold together all of these particulate components into a self-supporting structure. These mixed components are typically coated onto a metal foil which acts as a current collector in a battery. In addition, while binder materials and conductivity enhancers perform an important function, they do not contribute to the charge storage capacity of the electrode and therefore essentially dilute the charge storage capacity of the active material. Consequently, it is generally the objective of those skilled in the art to minimise the use of binders, conductivity enhancers and other non-active additives while still maintaining an electrode with suitable mechanical strength and electronic conductivity. Relative to larger particles, it is generally observed that smaller particles, due to their higher surface area compared to larger particles, require larger amounts of binder in the electrode to achieve a suitable level of mechanical robustness. Therefore, the use of larger particles has the advantage of requiring less binder, allowing higher charge storage capacities to be achieved.

[0042] In other embodiments, the multi-shelled hollow structures comprise microspheres.

[0043] In a second aspect, the present invention provides a method for forming multi-shelled hollow structures comprising metal oxide, the method comprising the steps of

- forming a solution by dissolving at least one metal-containing compound and organic material in a solvent,
- spray drying the solution to form composite particles comprising the at least one metal-containing compound and the organic material, and
- heating the composite particles by increasing temperature at a predetermined rate to form the multi-shelled hollow structures comprising metal oxide.

[0044] In the method of the present invention, the composite particles are formed by spray drying. The composite particles are then subjected to a separate heating or an annealing step in which the composite particles are subjected to increasing temperature at a predetermined rate. This converts the metal species or metal compound to a metal oxide whilst also removing the organic material from the particles.

[0045] Without wishing to be bound by theory, the present inventors have postulated that during the heating step in the non-equilibrium heat treatment, induced heterogeneous contraction dominates and is responsible for the formation of the metal oxide multi-shelled hollow structures. More specifically, the composite particles are not homogeneously heated during the heating/annealing; instead, there exists a temperature gradient (ΔT) along the radial direction of the particles. The ΔT leads to the first formation of a metal oxide shell at the surface of the composite particles. This shell is relatively rigid, and it can prevent the further contraction of the particles. Two forces of opposite directions exert at the interface of the composite core and the metal oxide shell. The contraction force (Fc) promotes the inward shrinkage of the core, while the adhesion force (Fa) induces the outward contraction. With a large ΔT, the Fc exceeds Fa, leading to the detachment of the core from the preformed shell. The abovementioned process (shell formation and core detachment) can be repeated several times until the ΔT become negligible. With a small ΔT, the Fa surpasses Fc, and the mass diffusion trend is reversed. That is, the inner core shrinks outwardly, leaving a cavity at the centre. As a result, multi-shelled hollow structures having a number of hollow shells.

[0046] In a further aspect, the present invention provides multi-shelled hollow structures comprising a metal oxide, the multi-shelled hollow structures comprising at least three hollow shells.

[0047] In some embodiments, the multi-shelled hollow structures comprise at least four hollow shells. In another embodiment, the multi-shelled hollow structures comprise four hollow shells. In some embodiments, the multi-shelled hollow structures suitably do not have a solid core. In other embodiments, the multi-shelled hollow structures have multiple hollow shells and a solid core within the inner shell.

[0048] The multi-shelled hollow structures of the present invention may be suitable for use as an active material on or in the anode of lithium ion batteries. Therefore, in a further aspect, the present invention provides an electrode material for a lithium ion battery anode, the electrode material including multi-shelled hollow structures in accordance with the present invention, as described herein.

[0049] In a further embodiment, a lithium ion battery using the anode of the present invention is provided. The multi-shelled hollow structures and the anode electrodes of the present invention can function as drop-in replacements for conventional anode active materials and anode electrodes. As such, no special processing of the active material or of the assembled anode is required and these components are compatible with the use of other conventional components used to make batteries such as electrolytes, separators, current collectors, cathodes and cell packing materials. Those skilled in the art will be well placed to select appropriate components in the construction of anode electrodes and battery devices using the multi-shelled hollow structures of the present invention.

[0050] The multi-shelled hollow structures of the present invention may also be suitable for removing contaminants, such as heavy metal ions, from solutions. Accordingly, in another aspect, the present invention provides a method for removing heavy metal ions dissolved in a solution, the method comprising contacting the solution with multi-shelled hollow structures in accordance with the present invention, as described herein.

[0051] The heavy metal ions that may be removed from the solution include arsenic, lead, cadmium, chromium, antimony, cobalt, copper, selenium and molybdenum.

[0052] The present inventors have also found that the multi-shelled hollow structures in the present invention may be used to remove polyanions, such as phosphate, from solution. Accordingly, in yet a further aspect, the present invention provides a method for removing polyanions from solution, the method comprising contacting the solution with multi-shelled hollow structures in accordance with the present invention, as described herein. The polyanions to be removed may be selected from arsenite, arsenate, phosphate. Other polyanions may also be removed.

[0053] The multi-shelled hollow structures used to remove heavy metal ions or phosphate from solution preferably comprise hematite (Fe_2O_3) chromium oxide, vanadium oxide, zinc iron ternary oxide and manganese-iron ternary oxide (Fe-Mn-O_x, such as ternary iron-manganese-oxides such as $MnFe_2O_4$ and $FeMn_2O_4$).

[0054] Where the multi-shelled hollow structures of the present invention are composed of iron oxide and have been designed for use in the removal of arsenic species from solution, the surface area of the material is typically lower that 100 m^2/g and more typically lower than 50 m^2/g. These values of surface area are significantly lower than those of commercial iron oxide materials used in the removal of arsenic species where surface areas of commercial materials can be in the range of 200-300 m^2/g. Such high surface areas are desired for maximising capacity to adsorb arsenic species as it is understood that arsenic adsorption is a surface phenomenon, and as such, larger surface areas impart a larger capacity for arsenic species removal. Without wishing to be bound by theory, the present inventors postulate that the higher arsenic adsorption capacities seen in the material of the present invention relative to commercial materials, despite the much lower surface areas measured, may result from the presence of the internal voids within each multi-shelled hollow structure particle which acts as a reservoir for sequestration of contaminant species. The concave shape of the inside walls of the multi-shelled hollow structures together with the internal void space may be acting to stabilise captured contaminant. In the case of arsenic species, adsorption to iron oxide is understood to occur by the build-up of multi-layers of arsenic species on the surface of the iron oxide according to the Freundlich isotherm model and it may be that the structure of the multi-shelled hollow materials of the present invention act to stabilise these multilayers of contaminants.

[0055] Adsorbent materials are often used in a particulate or granular form held within a cartridge or other container through which contaminated water requiring treatment is passed. To ensure the adsorbent material does not exit the container with the treated water, its exit is impeded by a mesh-like structure. In order for this to be effective, the particle size of the adsorbent material must be at least of a certain size. This is also important in ensuring reasonable flow rates through a treatment system since smaller particles tend to pack more tightly than larger particles, leaving lower amounts of interparticle void space for water to pass through thus requiring large back pressures to move water through the material.

[0056] The use of the adsorbent materials of the present invention is compatible with existing engineering solutions used in the water treatment industry. As such, the materials of the present invention have been designed to be a drop-in solution. Adsorbent material may be used as a pure powder, it may be attached to the surface of a carrier material or to a substrate or may be incorporated within an extruded or pressed porous filtration block such as those made from activated carbon particles. The choice of product format depends on the adsorbent particle size requirements of the application, the amount of arsenic to be removed and other factors. In large scale water utility or industrial arsenic removal processes it is common that the adsorbent material will be present as a collection of pure iron oxide particulates contained within a metal or plastic filtration tank through which contaminated water passes, as is commonly used in the art. Here, in order to minimise the frequency of adsorption media changeovers (replacing spent iron oxide media) pure iron oxide will be used to maximise absorption capacity. In residential applications the iron oxide absorption media of the present invention may be used in conjunction with water filter pitchers that are based on activated carbon. These devices typically only contain activated carbon and thus are not capable of adsorbing arsenic species from contaminated water. Particles of iron oxide could be included into the filtration media in order to provide an arsenic removal capability for these products. This would not lead to a significant decrease in the volume of activated carbon present in the filter (and hence a reduction in filtration capacity for other contaminants) as long as the arsenic adsorption capacity of the iron oxide was sufficiently high that only a small volume of material was required to remove arsenic to suitable levels. Here, the iron oxide could be included as a discrete powder mixed in with particles of activated carbon, as a discrete powder contained separately from the activated carbon, as particles fixed to the surface of the activated carbon particles, incorporated into a carbon block fabricated by extrusion or pressing or incorporated using other methods known to those skilled in the art. Optionally, the multi-shelled hollow structures or yolk shell structures could be packed in reactor beds for the treatment of industrial waste water.

[0057] The multi-shelled hollow structures of the present invention may also be suitable for oxidative or non-oxidative dehydrogenation of alkanes to alkenes. Accordingly, in a further aspect, the present invention provides a method for the oxidative or non-oxidative dehydrogenation of alkanes to alkenes, characterised in that multi-shelled hollow structures of the present invention are present during the oxidative or non-oxidative dehydrogenation of alkanes to alkenes.

[0058] Any of the features described herein can be combined in any combination with any one or more of the other features described herein within the scope of the invention.

[0059] The reference to any prior art in this specification is not, and should not be taken as an acknowledgement or any form of suggestion that the prior art forms part of the common general knowledge.

BRIEF DESCRIPTION OF DRAWINGS

[0060] Figure 1 shows a schematic illustration for the formation of α-Fe_2O_3 MSHSs in accordance with the postulated synthesis pathway;

[0061] Figure 2 shows an FESEM image of iron nitrate-sucrose composite microspheres formed after spray drying (sucrose/iron nitrate ratio: 10/10), but before annealing;

[0062] Figure 3 shows a TGA (thermogravimetric analyser) curve of the iron nitrate-sucrose composites (sucrose/iron nitrate ratio: 10/10) during heating thereof to elevated temperature.

[0063] Figure 4a shows a digital photo of the α-Fe_2O_3 MSHSs;

[0064] Figure 4b shows an XRD pattern of the α-Fe_2O_3 MSHSs;

[0065] Figures 5(a) to 5(f) show FESEM images (a, b) at an accelerating voltage of 5 and 15 kV, respectively. TEM images (c, d), SAED pattern (e), and HRTEM image (f) of α-Fe_2O_3 MSHSs (Sample 1);

[0066] Figures 6(a) to 6(f) show TEM images of Sample 2 (a and b, sucrose/iron nitrate ratio: 7.5/10), Sample 1 (c, sucrose/iron nitrate ratio: 10/10), Sample 3 (d and e, sucrose/iron nitrate ratio: 15/10), and Sample 4 (f, sucrose/iron nitrate: 20/10);

[0067] Figures 7(a) to 7(e) show FESEM (a – c) and TEM (d, e) images of α-Fe_2O_3 hollow structures (Sample 5, temperate ramp rate: 0.5 °C/min). For a and b, the accelerating voltage is 5 kV; for c, the accelerating voltage is 15 kV;

[0068] Figures 8(a) to 8(e) show FESEM (a – c) and TEM (d, e) images of α-Fe_2O_3 hollow structures (Sample 6, temperature ramp rate: 5 °C/min). For (a) and (b), the accelerating voltage is 5 kV; for (c), the accelerating voltage is 15 kV;

[0069] Figures 9(a) to 9(d) show TEM images of α-Fe_2O_3 hollow structures using glucose (a and b, Sample 7) and PVA (c and d, Sample 8) as the organic species;

[0070] Figures 10(a) to 10(e) show FESEM (a, b), TEM (c, d), SAED (e) and HRTEM (f) images of $ZnFe_2O_4$ yolk-shell structures;

[0071] Figure 11 shows XRD pattern of the $ZnFe_2O_4$ yolk-shell structures;

[0072] Figure 12 shows CVs (cyclic voltrammetry) of α-Fe_2O_3 MSHSs for the initial three cycles at a rate of 0.1 mA s^{-1};

[0073] Figures 13(a) to 13(d) show (a) Representative charge-discharge profiles of α-Fe_2O_3 MSHSs at a current density of 400 mA g^{-1} in the voltage window of 0.05 – 3.0 V; (b) cycling performance of α-Fe_2O_3 MSHSs at a current density of 400 mA g^{-1}; (c) representative charge-discharge profiles of α-Fe_2O_3 MSHSs at different current densities (100 – 3200 mA h g^{-1}); (d) rate performance of α-Fe_2O_3 MSHSs. For a and b, current density of the first two cycles are 50 mA g^{-1};

[0074] Figure 14 shows Coulombic efficiency *vs.* cycle number;

[0075] Figure 15 shows TEM images of Cr_2O_3 multi-shelled hollow spheres formed in accordance with an embodiment of the present invention;

[0076] Figure 16 shows TEM images of V_2O_5 yolk-shell structures formed in accordance with an embodiment of the present invention;

[0077] Figure 17 shows XRD pattern of V_2O_5 yolk-shell structures; and

[0078] Figure 18 shows a TEM image of α-Fe_2O_3 MSHSs prepared by calcining an iron nitrate-sucrose composite at 600 °C for 5 hours in air.

[0079] Figure 19 shows a drinking water treatment device.

[0080] Figure 20 illustrates the arsenic removal capabilities of α-Fe_2O_3 multi-shelled hollow structures when used in the drinking water treatment device of Figure 19.

[0081] Figures 21(a) to 21(g) show TEM images of α-Fe_2O_3 multi-shelled hollow structures with an iron citrate precursor using sucrose as the organic species.

[0082] Figure 22 illustrates the adsorption of anions other than arsenic anions using α-Fe_2O_3

multi-shelled hollow structures.

[0083] Figure 23 illustrates granular particles produced using α-Fe_2O_3 multi-shelled hollow structure material.

EXAMPLES

[0084] The examples mainly relate to the preparation of α-Fe_2O_3 multi-shelled hollow structures.

[0085] The α-Fe_2O_3 MSHSs hollow microspheres were prepared by a spray drying method followed by annealing in air. In a typical synthesis (Sample 1, see Table 1), $Fe(NO_3)\cdot 9H_2O$ (10 mmol) and sucrose (10 mmol) were dissolved in H_2O (100 mL) to form a clear solution. The resulting solution was then spray dried using a Buchi mini spray drier B-290 at an inlet temperature of 220 °C, an aspirator rate of 100 %, a rotameter setting of 60 mm, and a pump rate of 5 % (1.5 mL/min). Nitrogen was used as the drying gas. These settings resulted in an outlet temperature of ~ 130 °C. The spray dried samples (iron nitrate-sucrose composite) were then annealed in air at 400 °C for 5 hours with a temperature ramp rate of 2 °C/min. To study the influence of synthesis parameters on the structures, a series of samples were prepared by adjusting the feeding ratio of reagents, the temperature ramp rate, and the choices of organic matrices. The detailed synthesis conditions for all samples are listed in Table 1.

Table 1. Synthesis conditions for α-Fe_2O_3 hollow structures/nanostructures.

Sample Name	Organic Species	Iron Nitrate	Temperature ramp rate
Sample 1	Sucrose, 10 mmol	10 mmol	2 °C/min
Sample 2	Sucrose, 7.5 mmol	10 mmol	2 °C/min
Sample 3	Sucrose, 15 mmol	10 mmol	2 °C/min
Sample 4	Sucrose, 20 mmol	10 mmol	2 °C/min
Sample 5	Sucrose, 10 mmol	10 mmol	0.5 °C/min
Sample 6	Sucrose, 10 mmol	10 mmol	5 °C/min
Sample 7	Glucose, 20 mmol	10 mmol	2 °C/min
Sample 8	Polyvinyl alcohol, 4 g	10 mmol	2 °C/min

[0086] Characterization

[0087] X-ray diffraction (XRD) patterns were collected on a German Bruker D8 Advanced X-Ray Diffractometer with Ni filtered Cu Kα radiation (40 kV, 30 mA). Field emission scanning electron microscopy (FESEM) images were obtained on a JEOL JSM 7800 microscope with an accelerating voltage of 5.0 or 15.0 kV. Transmission electron microscopy (TEM) images were taken on Tecnai F20 (200 kV) and JEOL 1010 (100 kV) microscopes. Thermo gravimetric analysis (TGA) was carried out on a TGA/DSC1 STAR© System under air flow (25 – 1000 °C, 5 °C/min). Nitrogen adsorption isotherms were measured at 77 K using a TriStar II Surface Area and Porosity analyser (Micromeritics). The samples were degassed under vacuum for 6 hours at 200 °C before analysis. BET surface area was calculated from the adsorption branch in relative pressure (p/p_0) range of 0.05 – 0.30.

[0088] Electrochemical Measurement

[0089] The electrochemical measurements were carried out in homemade two-electrode Swagelok type cells. The working electrode is consisted of active material, conductive acetylene black, and polyvinylidene fluoride binder in a weight ratio of 70:20:10. Lithium chips were used as both the counter electrode and reference electrode. 1 M $LiPF_6$ in a mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate (1:1:1 in volume) was used as the electrolyte. Cell assembly was carried out in an Ar-filled glovebox with moisture and oxygen concentrations below 1.0 ppm. Cyclic voltammetry (CV) measurements were performed on a Solartron 1480 MultiStat instrument. The galvanostatic charge-discharge tests were performed on a MTI 8 Channels Battery Analyzer.

[0090] The synthesis of α-Fe_2O_3 MSHSs is based on a simple spray drying method followed by annealing in air. The first step involves the preparation of iron nitrate-sucrose composite microspheres by spray drying; while the second step is annealing the composite spheres in air at 400 °C. The non-equilibrium heat treatment induced heterogeneous contraction dominates the second step and is responsible for the formation of the α-Fe_2O_3 MSHSs. More specifically, the iron nitrate-sucrose microspheres are not homogeneously heated during the annealing; instead, there exists a temperature gradient (ΔT) along the radical direction. The ΔT leads to the first formation of a α-Fe_2O_3 shell at the surface of the composite spheres. This shell is relatively rigid, and it can prevent the further contraction of the microspheres. Two forces of opposite directions exert at the interface of the composite core and α-Fe_2O_3 shell. The contraction force (Fc) promotes the inward shrinkage of the core, while the adhesion force (Fa) induces the outward contraction. With a large ΔT, the Fc exceeds Fa, leading to the detachment of the core from the preformed shell. The abovementioned process (shell formation and core detachment) can be repeated for several times until the ΔT become negligible. With a small ΔT, the Fa surpasses Fc, and the mass diffusion trend is reversed. That is, the inner core shrinks outward, leaving a cavity at the centre.

[0091] A schematic diagram showing the postulated synthesis pathway is show in Figure 1. Figure 2 shows an FESEM image of the iron nitrate-sucrose composite particles formed after spray drying of the iron nitrate-sucrose solution in the spray drier.

[0092] The composite iron nitrate-sucrose particles were then heated. Figure 3 shows a TGA (thermogravimetric analyser) curve of the iron nitrate-sucrose composites (sucrose/iron nitrate mole ratio: 10/10). As can be seen from figure 3, the weight of the particles decreases as temperature increases, due to decomposition of the iron nitrate to iron oxide and due to decomposition and calcination of the sucrose. It is believed that the sucrose is eventually converted to carbon dioxide, which is removed from the particles. This can also be seen from figure 3, no further weight loss is identified after the temperature reaches 400°C, indicating that further heating above 400°C should not be required to fully form the α-Fe_2O_3 multi-shelled hollow particles.

[0093] Well-developed α-Fe_2O_3 MSHSs can be synthesized in a large scale using inexpensive iron nitrate and sucrose as the precursors (Figure 4a). The as-prepared product is first characterized by XRD to gain insight into the crystallographic structure. As shown in Figure 4b, all the diffraction peaks can be well indexed to rhombohedra phase α-Fe_2O_3 (JCPDS Card No. 33-0664), also known as hematite, with a $R\bar{3}c$ space group. No other peaks can be detected, indicating the high purity of the products. The relatively broad diffraction peaks suggesting the nanocrystalline characteristic of the sample. By applying Scherrer equation on the strongest (104) diffraction peak, the average crystallite size is determined to be 24 nm.

[0094] The morphology and structure of the products were examined by SEM and TEM. As can be seen from Figure 5(a) and 5(b), the products consists of microspheres with a size in the range of 400 – 2000 nm. With a relatively low accelerating voltage of 5 kV (Figure 5(a)), one can find that the microspheres are not perfectly smooth; instead, wrinkles can be observed on the surface. From the broken part of a microsphere, an inner core particle is exposed, indicating the microspheres actually have a yolk-shell or multi-shell structure. With a high accelerating voltage of 15 kV, the penetration capability of the electrons in SEM is greatly enhanced. Thus, the inner cores can be clearly discerned even though the microspheres are intact (Figure 5(b)). Low magnification TEM images (Figure 5(c) and 5(d)) undisputedly demonstrate the microspheres have a multi-shelled structure and most of the spheres have four shells. The thickness of the shell is around 20 nm, which is generally agrees with the crystallite size determined from XRD. The selected area electron diffraction (SAED) pattern (Figure 5(e)) of the microspheres shows a series of concentric rings, which can be assigned to the (012), (104), (110), (113), (024) and (116) diffractions of α-Fe_2O_3, respectively. A typical high resolution TEM (HRTEM) image is shown in Figure 5(f), where the (012) lattice fringes of α-Fe_2O_3 can be clearly observed.

[0095] This unique multi-shelled hollow structure gives rise to a relatively high surface area of 17.2 m^2 g^{-1} and pore volume of 0.1 cm^3 g^{-1}.

[0096] The effect of iron nitrate/sucrose on the structure of the products has been studied (Figure 6(a) to 6(f)). The optimised sucrose/iron nitrate ratio (mole ratio) for the fabrication of α-Fe_2O_3 MSHSs is found to be in the range of 7.5/10 – 10/10 (Figure 6(a) – 6(c)). With a sucrose/iron nitrate of less than 5/10, no iron nitrate-sucrose composite spheres can be formed by spray drying (data not shown). With a sucrose/iron nitrate of more than 15/10, α-Fe_2O_3 nanosheets rather than hollow spheres are formed (Figure 6(d) – 6(f)).

[0097] According to the heterogeneous contraction mechanism, the temperature ramp rate may also play an important role on the morphology and structure of the products: a low ramp rate will lead to a small ΔT, and thus fewer shells; while a high ramp rate will result in a high ΔT, and thus more shells. With a low ramp rate of 0.5 °C/min, single-shelled hollow spheres and yolk-shell structures are formed (Figure 7). With a high ramp rate of 2 and 5 °C/min, multi-shelled hollow spheres are formed (Figure 8). Compared to sample 1 (Figure 5) with a ramp rate of 2 °C/min, sample 6 with a ramp rate of 5 °C (Figure 8) shows more broken spheres.

[0098] Besides sucrose, other organic species, such as glucose (Figure 9(a) and 9(b)) and polyvinyl alcohol (Figure 9(c) and 9(d)) can also be utilized as the matrix to synthesize α-Fe_2O_3 hollow spheres. This strategy is not limited to the fabrication of α-Fe_2O_3 hollow spheres. As another example, $ZnFe_2O_4$ yolk-shell structures (Figure 10 and 11) can also be fabricated by this approach by simply replacing one third of the iron nitrate with zinc nitrate.

[0099] Figures 21a to 21g illustrate the use of different quantities of sucrose as the organic species utilized as the matrix to synthesize α-Fe_2O_3 hollow spheres having an iron citrate precursor. In the synthesis of the α-Fe_2O_3 hollow spheres in Figures 21a to 21g, 10 mmol of iron citrate was dissolved in 100ml of water to form a clear solution. In Figure 21a no sucrose was added to the solution, while in Figure 21b 2.5 mmol of sucrose was added, in Figure 21c 5 mmol was added, in Figure 21d 7.5 mmol was added, in Figure 21e 10 mmol was added, in Figure 21f 12.5 mmol was added and in Figure 21g 15 mmol was added.

[00100] The resulting solution was then spray dried using a Buchi mini spray drier B-290 using air as the drying gas. The as-made samples were then annealed in air at 400°C for 5 hours with a temperature ramp rate of 2°C/hour, with the resulting iron oxide structures illustrated in Figures 21a to 21g. High arsenic absorption capacity was confirmed for these α-Fe_2O_3 structures produced from the iron citrate precursor.

[00101] To study the lithium storage capabilities of the α-Fe_2O_3 MSHSs, CV and galvanostatic charge/discharge cycling were carried out based on the half-cell configuration. The CVs for the initial three cycles at a rate of 0.1 mV s^{-1} are shown in Figure 12. Three cathodic peaks can be observed in the first cycle. The first peak centred at 1.58 eV can be attributed to the intercalation of lithium into the crystal structure of α-Fe_2O_3; the second peak centred at 0.93 eV can be attributed to the reduction of Fe^{3+} to Fe^{2+}; and the third peak centred at 0.58 eV can be attributed to the reduction of Fe^{2+} to Fe and the irreversible reduction of the electrolyte. In the first anodic process, only one broad peak located between 1.5 and 2.0 V can be observed, corresponding to the oxidation of Fe to Fe^{3+}. From the second cycle onward, a pair of broad cathodic/anodic peaks can be observed and the CV curves generally overlaps, suggesting a good reversibility the redox reaction ($Fe^{3+} + 3e^- \leftrightarrow Fe$).

[00102] The cycling performance of the α-Fe_2O_3 electrode was evaluated by activating the half cells at 50 mA g^{-1} for two cycles and then cycling at 400 or 1600 mA g^{-1}. At a current of $50mAg^{-1}$, the α-Fe_2O_3 MSHSs delivers an initial discharge capacity of 1443 mA h g^{-1} and a charge capacity of and 1067 mA h g^{-1}, respectively (Figure 13a). After the activation process, a high and stable capacity of ~ 1000 and 900 mA h g^{-1} can be achieved at a current of 400 and 1600 mA g^{-1} (Figure 13b), respectively. The coulombic efficiency for the first cycle is around 75%, while it stabilizes at ~ 98% after the activation process (Figure 14).

[00103] The rate performance of the α-Fe_2O_3 was investigated by cycling the material at various currents ranging from 100 to 3200 mA g^{-1} for 5 cycles. Representative charge-discharge profiles (the third cycle at each rate) are shown in Figure 13c. As the current density increases from 100 to 200, 400, 800, 1600 and 3200 mA g^{-1}, the capacity only decreases slightly from 1228 to 1193, 1102, 1013, 913 and 784 mA h g^{-1}(Figure 13c and 13d), indicating the excellent rate capability of the α-Fe_2O_3 MSHSs. After reaching its highest value, that is 3200 mA g^{-1}, the current density is reduced to 200 mA g^{-1} gradually. A capacity of 1176 mA h g^{-1} can be recovered at 200 mA g^{-1}, which is 98.6 % of the capacity at the same current density before the high rate measurement.

[00104] Notably, the electrochemical performances of the α-Fe_2O_3 MSHSs are superior or at least comparable to those of high-performance Fe_2O_3-based anode materials reported recently, such as α-Fe_2O_3 nanorods, α-Fe_2O_3 hollow spheres, Fe_2O_3 decorated carbon nanotubes, and Fe_2O_3-reduced graphene oxide nanocomposites. The enhanced electrochemical performances can be attributed to the unique structural characteristics of the α-Fe_2O_3 MSHSs. The permeable and thin shells greatly shorten the distances for Li^+ diffusion; the void space effectively accommodates the drastic volume change and alleviates the strain during Li^+ insertion/extraction. All these features contribute to the stable high-rate performance of the α-Fe_2O_3 MSHSs.

EXAMPLE - Nanoporous hematite for As removal

[00105] The properties of nanoporous hematite were also investigated for arsenic removal. Without wishing to be bound by theory, the present inventors have hypothesized that the existence of voids within layers might accommodate arsenic species for adsorption purpose.

[00106] $Na_2HAsO_4.7H_2O$ (Sigma Aldrich) and $NaHAsO_2$ (Ajax Finekem) were used as As(V) and As(III) sources, respectively. 0.01M HCl and 1×10^{-4}M NaOH were used for pH adjustment. Distilled water was used throughout the experiment.

Batch experiments:

[00107] A solution containing 400 ppm As(III) was prepared by dissolving 693.5 mg of $NaHAsO_2$ in 1 L H_2O. Consequently, 1.65 g of $Na_2HAsO_4.7H_2O$ was dissolved in 1 L H_2O to make 400 ppm of As(V) solution. Serial dilutions were performed to obtain arsenic concentrations of 200ppm, 1 ppm, and 50ppb for both As(V) and As(III) solutions. A dosage 20 mg of nanoporous hematite was added into each 50 mL solution. All solutions were shaken for 24 h at room temperature at a speed of 200 rpm.

[00108] WAGTECH arsenic kit™ was used to quantify the amount of arsenic adsorbed. The filter paper was calibrated prior to each arsenic quantification.

[00109] The removal at both high and low As concentrations are presented below.

Table 2. Summarized results of As removal at high concentrations using nanoporous Fe_2O_3

t (h)	**C_0 (ppm)**	**Q_e (mg/g)**	
		As(III)	As(V)
3	200	375	437
		-	101.4[a]
	400	575	712
		-	137.5[b]
24	400	750	862

Table 3. Summarized results of As(V) removal at low concentrations

pH	Initial Conc (ppb)	Final Conc (ppb)
8.5 (8.46-8.53)	50	0
6.5 (6.47-6.51)	50	0
7.0 (6.96-7.04)	50	0
7.0 (6.97-7.02)	1000	39
Unadjusted (pH = 5.93 – 8.21)	1000	8

All pH values were recorded under stirring. All measurements were in duplicate

Table 4. Summarized results of As(III) removal at low concentrations

pH	Initial Conc (ppb)	Final Conc (ppb)
8.5 (8.58-8.51)	50	0
6.5 (6.47-6.51)	50	0
8.5 (8.49)	1000	32
Unadjusted (pH = 6.04 - 8.63)	1000	39

All pH values were recorded under stirring. All measurements were in duplicate

[00110] From the above tabulated results, it can be concluded that nanoporous hematite is beneficial for arsenic removal, as it can lower down the As(V) concentration from 1ppm to 8ppb (table 3), which is below the stringent discharge limit.

[00111] It is expected that the α-Fe_2O_3 multi-shelled hollow structures made in accordance with the present invention will also be able to remove other heavy metal ions, such as lead, cadmium, chromium, antimony and molybdenum, as well as removing phosphate ions from solution.

[00112] To demonstrate the effectiveness of nanoporous hematite in arsenic removal in the case that the hematite is used in combination with an activated carbon-based water treatment system, nanoporous hematite was used as an additive to the filter media of a standard activated

carbon-based water purification system. The addition of the nanoporous hematite conveys an arsenic removal capability on the system enabled by the hematite.

[00113] The test is illustrated in Figure 19. In this test, a commercial water filter pitcher 10 (Brita® Maxtra) was used as the standard water filter device. The standard media 11 in this device is composed of activated carbon and ion exchange resin with a total mass of 30g. For the device modified for arsenic removal, 0.1g of α-Fe_2O_3 multi-shelled hollow structures 12 made in accordance with the present invention were added to the 30g of standard media 11 by mixing the α-Fe_2O_3 multi-shelled hollow structures 12 into the standard media 11.

[00114] An aqueous solution 13 containing 100ppb As(V) was fed through both standard filter (not shown) and a modified filter 14 under gravity, and the concentration of As(V) was measured in the effluent 15. As illustrated in Figure 20, it was found that the standard filter (not shown) reduced As(V) concentration in the water from 100ppb to 40ppb with 1 litre of water poured through the filter.

[00115] By contrast, the modified filter 14 containing 0.1g of α-Fe_2O_3 multi-shelled hollow structures 12 reduced the As(V) concentration in the effluent 15 from 100ppb to around 0ppb.

Example – Adsorption of anions other than arsenic anions

[00116] In Figure 22 there is illustrated the adsorption of oxyanions other than arsenic oxyanions using α-Fe_2O_3 multi-shelled hollow structures synthesised in accordance with the present invention. This Figure demonstrates the ability of the non-arsenic anions to complete for adsorption sites on the iron oxide structures and, in doing so, reduce the capacity of the iron oxide to adsorb arsenic species.

[00117] In this Example, the As(III) and As(V) adsorption capacity of the α-Fe_2O_3 multi-shelled hollow structures was studied using 400ppm arsenic contaminated waters that also contained additional non-arsenic anions. The non-arsenic anions were present at a concentration of 1g/L and were provided by the addition of Na_2SO_4, Na_3PO_4, Na_2CO_3, and $NaSiO_3$. α-Fe_2O_3 multi-shelled hollow structures were present in the solutions at a dosage of 20mg per 50mL of solution.

[00118] The effect of the addition of competing anions on As(III) and As(V) adsorption performance is illustrated in Figure 22. In all cases, the addition of the competing anions reduces the ability of the α-Fe_2O_3 multi-shelled hollow structures to adsorb arsenic anions, thereby demonstrating that the α-Fe_2O_3 multi-shelled hollow structures also adsorb non-arsenic

anions. The decrease in the adsorption of arsenic anions due to the presence of competing anions is summarised in Table 5 below.

Table 5 Summarized results of reduced arsenic anion adsorption due to competing anions

Anions	**% Decrease** **As(III)**	**% Decrease** **As(V)**
Sulfate	23	11
Phosphate	36	20
Silicate	51	48
Carbonate	15	11

Example – Production of Cr_2O_3 multi-shelled hollow spheres.

[00119] The method of the present invention has been used to form Cr_2O_3 multi-shelled hollow spheres. Figure 15 shows TEM images of the Cr_2O_3 multi-shelled hollow spheres that were formed. Multiple shells can be clearly seen.

Example – Production of V_2O_5 yolk-shell structures.

[00120] Figure 16 shows TEM images of V_2O_5 yolk-shell structures formed in accordance with an embodiment of the present invention. Figure 17 shows XRD pattern of V_2O_5 yolk-shell structures. Again, multiple shells can be seen.

Example – Formation of α-Fe_2O_3 MSHSs prepared by calcining an iron nitrate-sucrose composite.

[00121] Figure 18 shows a TEM image of α-Fe_2O_3 MSHSs prepared by calcining an iron nitrate-sucrose composite at 600 °C for 5 hours in air. As can be seen, a multi shelled material has been obtained, showing that higher calcination temperatures are not detrimental to formation of the multi-shelled hollow structures. However, it will be appreciated that calcination to temperatures above the minimum temperature at which the organic material has been removed and the metal oxide phase(s) has been fully formed may not be required unless the higher temperature results in improved crystallinity in the material.

[00122] Embodiments of the present invention provide a facile method for the high-yield and large-scale synthesis of α-Fe_2O_3 multi-shelled hollow spheres (MSHSs) by spray drying. The resultant α-Fe_2O_3 hollow spheres exhibit high specific capacity, excellent rate capability and cycling stability. The method can also be used to make hollow spheres of other metal oxides. They can also be used to remove contaminants, such as heavy metals and polyanions, from solutions, such as water streams.

[00123] **Example – Synthesis of granular particles based on α-Fe_2O_3 particles**

[00124] In this Example, granules were produced using the extrusion granulation method. 0.5g of α-Fe_2O_3 multi-shelled hollow spheres were mechanically mixed with wet aluminium hydroxide gel. The resulting uniform mixture was extruded through a 20 mesh sieve to produce granules that were dried at 50°C - 100°.

[00125] The final α-Fe_2O_3 weight percentage in the granules was between 60% and 95% and this value was controlled by the proportion of aluminium hydroxide gel added to the α-Fe_2O_3 multi-shelled hollow spheres.

[00126] The arsenic absorption capacity of the granulated α-Fe_2O_3 multi-shelled hollow spheres was not reduced compared to the α-Fe_2O_3 multi-shelled hollow spheres primary particles. As illustrated in Figure 23, the particle size of the granulated material 20 was in the order of millimetres in length.

[00127] In the present specification and claims (if any), the word 'comprising' and its derivatives including 'comprises' and 'comprise' include each of the stated integers but does not exclude the inclusion of one or more further integers.

[00128] Reference throughout this specification to 'one embodiment' or 'an embodiment' means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, the appearance of the phrases 'in one embodiment' or 'in an embodiment' in various places throughout this specification are not necessarily all referring to the same embodiment. Furthermore, the particular features, structures, or characteristics may be combined in any suitable manner in one or more combinations.

[00129] In compliance with the statute, the invention has been described in language more or less specific to structural or methodical features. It is to be understood that the invention is not limited to specific features shown or described since the means herein described comprises

preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims (if any) appropriately interpreted by those skilled in the art.

CLAIMS

1. A method for forming multi-shelled hollow structures comprising metal oxide, the method comprising the steps of:

- forming a solution containing at least one dissolved metal compound and at least one organic compound,
- spray drying the solution to form composite particles containing at least one metal species and organic material, and
- heating the composite particles by increasing temperature at a predetermined rate to form the multi-shelled hollow structures comprising metal oxide.

2. A method according to claim 1 wherein the solution is formed by dissolving a metal compound and at least one organic compound in water.

3. A method according to claim 1 or claim 2 wherein the at least one dissolved metal compound is formed by dissolving a metal-containing compound in a solvent.

4. A method according to any one of claims 1 to 3 wherein the at least one dissolved metal compound comprises a metal nitrate, a metal chloride, a metal sulphate, a metal acetate, a metal alkoxide, a metal citrate, a metal lactate, a metal gluconate, a metal oxalate or an ammonium-metal compound.

5. A method according to any one of the preceding claims wherein the at least one dissolved metal compound comprises two or more dissolved metal compounds.

6. A method according to claim 5 wherein the two or more dissolved metal compounds comprise an iron compound and another metal compound.

7. A method according to any one of the preceding claims wherein the organic compound comprises an organic compound that can be removed by calcination.

8. A method according to any one of the preceding claims wherein the organic material comprises sucrose, glucose, oxalic acid, polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene glycol or citric acid.

9. A method according to any one of the preceding claims wherein the temperature of the composite particles is increased at a predetermined rate by increasing the temperature at a constant rate.

10. A method according to any one of the preceding claims wherein the multi-shelled hollow structures are maintained at a high temperature for a period of time in order to improve the crystallinity of the structures.

11. A method according to any one of the preceding claims wherein the metal oxide formed in the multi-shelled hollow structures is hematite.

12. A method for forming multi-shelled hollow structures comprising metal oxide, the method comprising the steps of

- forming a solution by dissolving at least one metal-containing compound and organic material in a solvent,
- spray drying the solution to form composite particles comprising the at least one metal-containing compound and the organic material, and
- heating the composite particles by increasing temperature at a predetermined rate to form the multi-shelled hollow structures comprising metal oxide.

13. A method according to claim 12 wherein the multi-shelled hollow structures comprise at least three hollow shells.

14. A method according to claim 12 or claim 13 wherein the multi-shelled hollow structures do not have a solid core.

15. Multi-shelled hollow structures comprising a metal oxide, the multi-shelled hollow structures comprising at least three hollow shells.

16. Multi-shelled hollow structures according to claim 15 wherein the at least three hollow shells comprise shells of decreasing size located within larger shells.

17. Multi-shelled hollow structures according to claim 15 or claim 16 wherein all of the at least three shells are hollow.

18. Multi-shelled hollow structures according to claim 15 or claim 16 wherein the structures further comprise a solid core.

19. Multi-shelled hollow structures according to any one of claims 15 to 18 wherein the structure comprise particles having a size falling within the range of 200nm to 4000nm.

20. Multi-shelled hollow structures according to any one of claims 15 to 19 wherein the metal oxide comprises hematite.

21. A fused aggregate of multi-shelled hollow structures comprising a plurality of particles as formed by the method claimed in any one of claims 1 to 14 or as claimed in any one of claims 15 to 20 joined to other particles to form an aggregate.

22. A method for forming the aggregate of claim 21 comprising the steps of mixing the multi-shelled hollow structures with a metal hydroxide or a precursor to a metal hydroxide to form a mixture, and processing the mixture to form aggregate particles.

23. An electrode material for a lithium ion battery anode, the electrode material including multi-shelled hollow structures as claimed in claims 15 to 20, or as formed by the method of any one of claims 1 to 14.

24. A method for removing heavy metal ions dissolved in a solution, the method comprising contacting the solution with multi-shelled hollow structures as claimed in claims 15 to 20, or as formed by the method of any one of claims 1 to 14.

25. A lithium ion battery comprising the electrode material as claimed in claim 23.

26. A water filter system for the removal of contaminants, the water filter system comprising multi-shelled hollow structures as claimed in claims 15 to 20 or as formed by the method of any one of claims 1 to 14, or the fused aggregates of claim 21 or as formed by the method of claim 22, wherein the multi-shelled hollow structures or the fused aggregates are optionally present with activated carbon.

27. A water filter system according to claim 26 wherein the multi-shelled hollow structures or the fused aggregates and the activated carbon, if present, are in the form of a powder.

28. A water filter system according to claim 26 wherein the multi-shelled hollow structures or the fused aggregates are attached to the surface of a carrier material or to a substrate.

29. A water filter system according to claim 26 wherein the multi-shelled hollow structures or the fused aggregates are incorporated within an extruded or pressed carbon filter block.

30. A method for the oxidative or nonoxidative dehydrogenation of alkanes to alkenes, characterised in that multi-shelled hollow structures as claimed in claims 15 to20, or as formed by the method of any one of claims 1 to 14, are present during the oxidative or nonoxidative dehydrogenation of alkanes to alkenes.

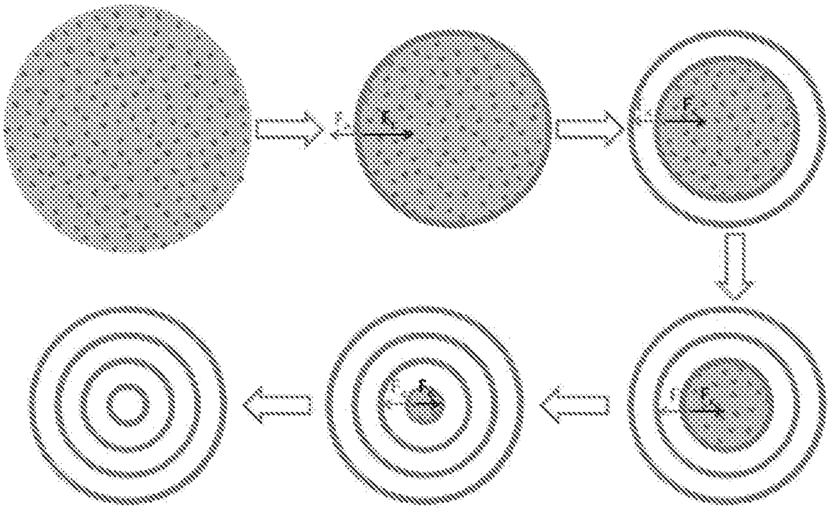


Figure 1

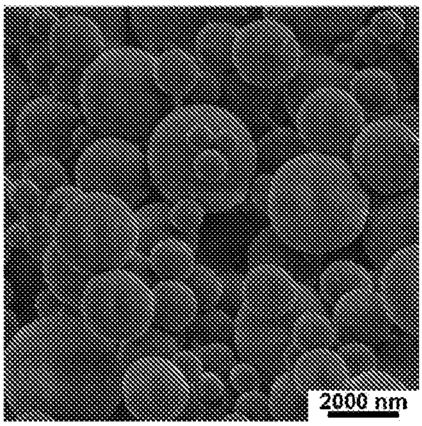


Figure 2

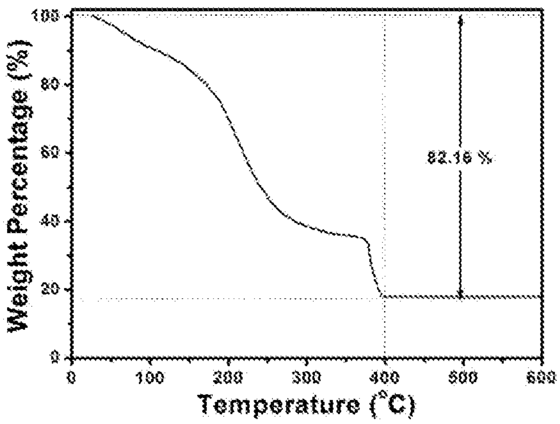
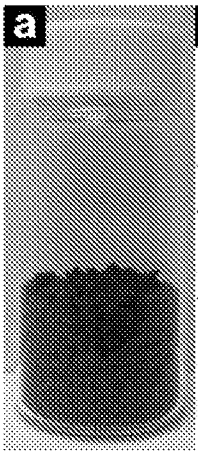


Figure 3



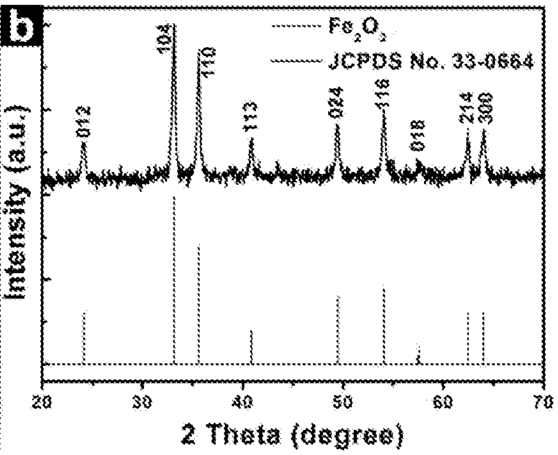
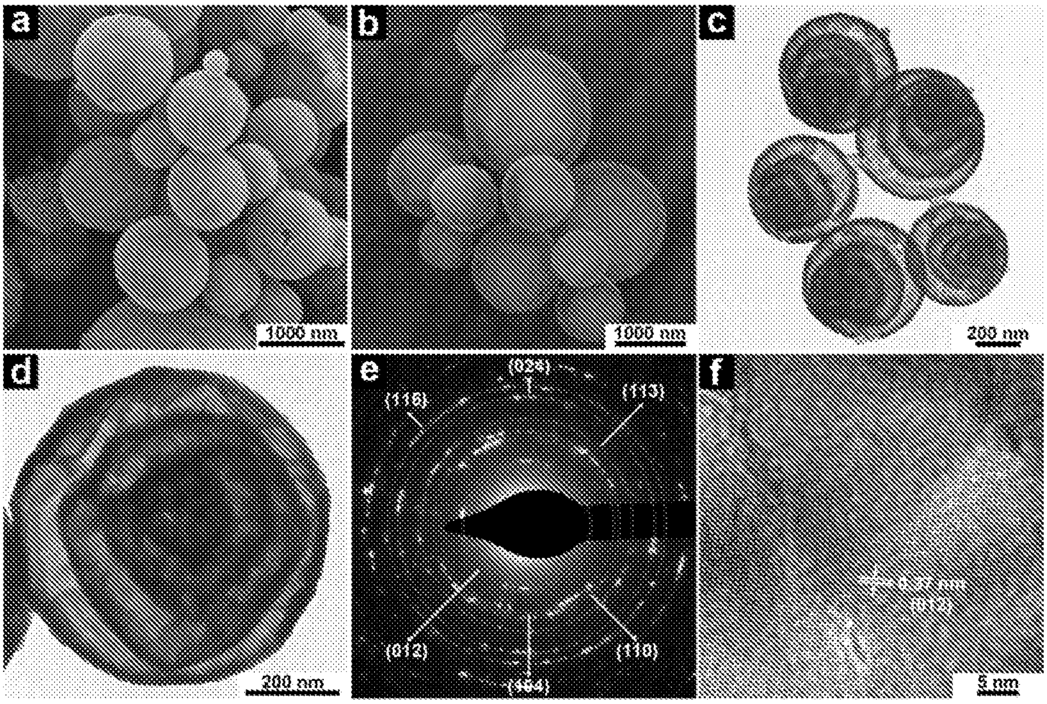
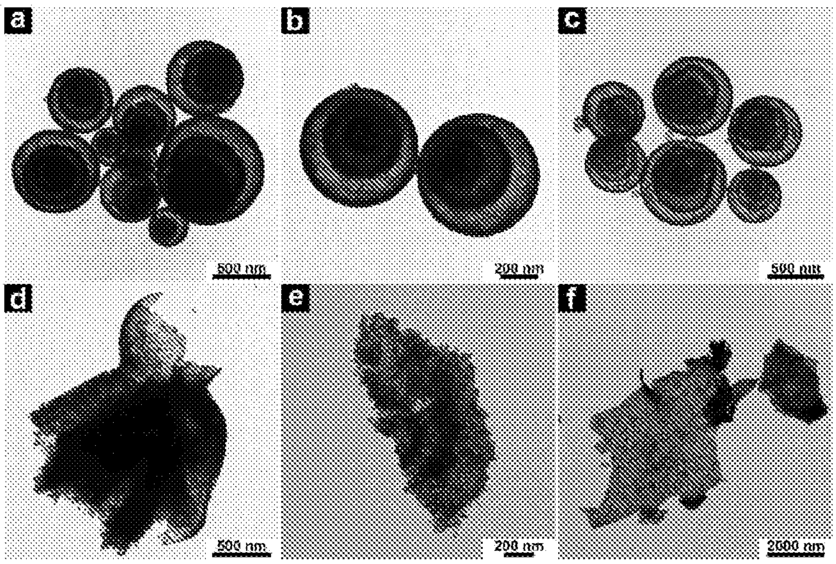


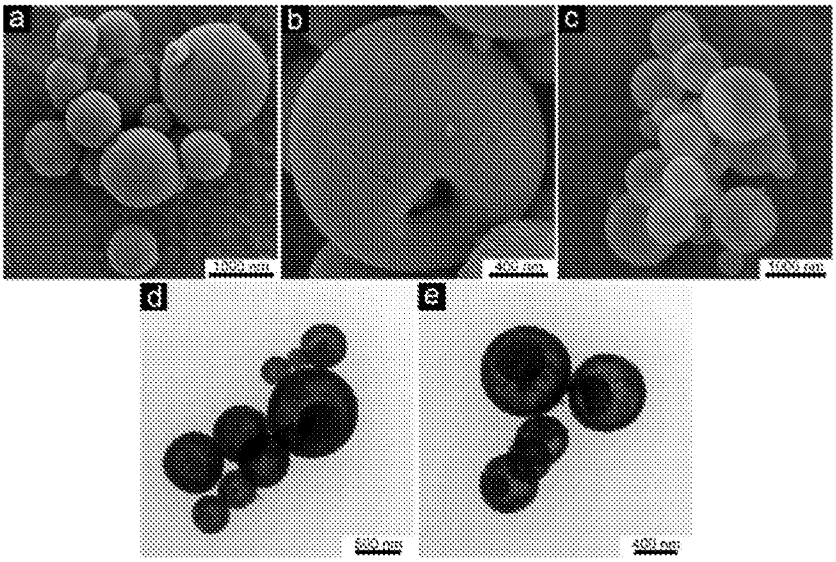
Figure 4a Figure 4b



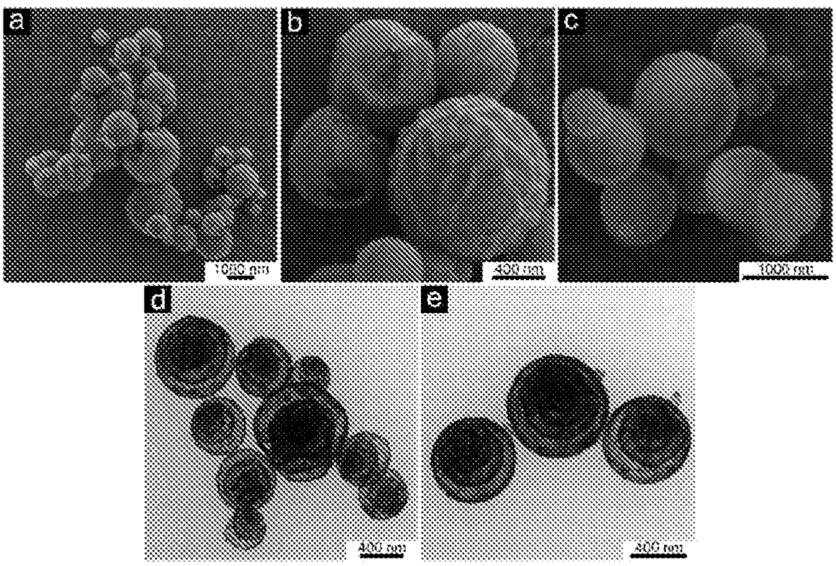
Figures 5a to 5f



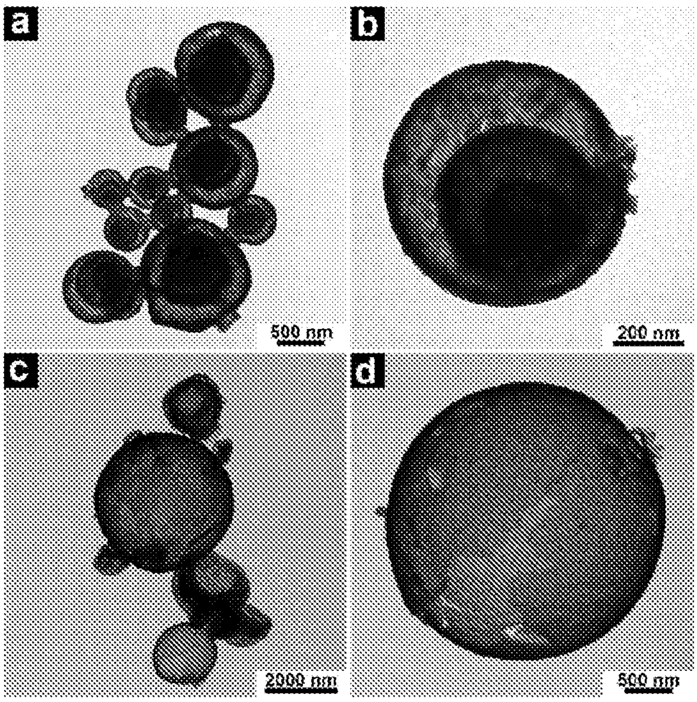
Figures 6a to 6f



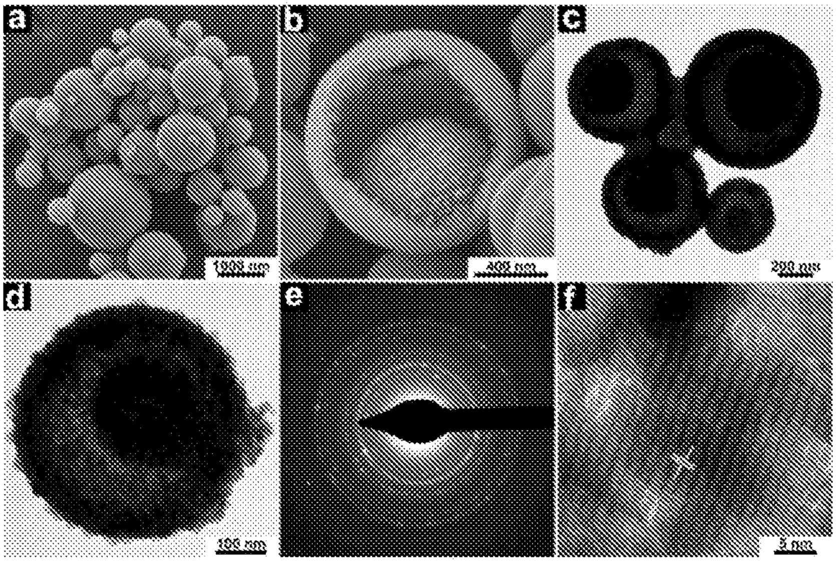
Figures 7a to 7e



Figures 8a to 8e



Figures 9a to 9d



Figures 10a to 10e

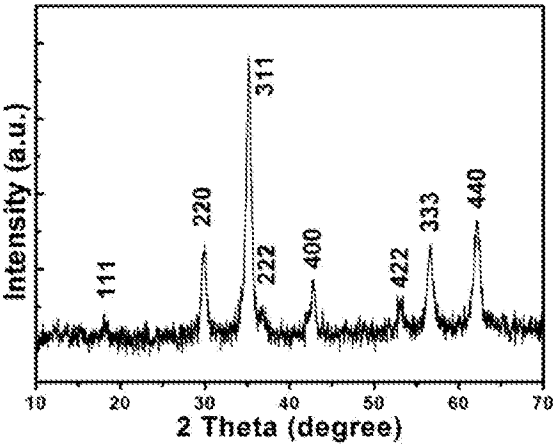


Figure 11

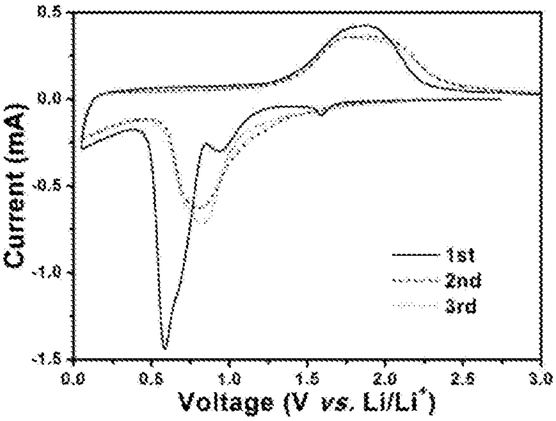
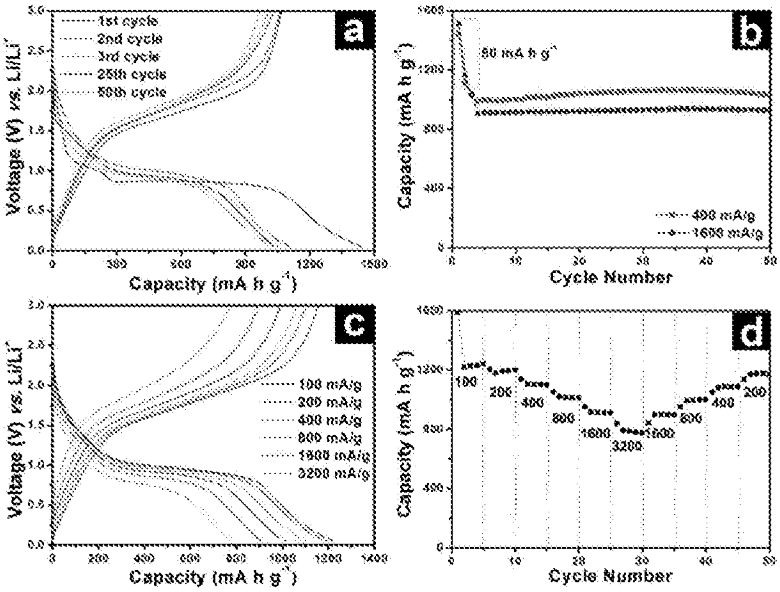


Figure 12



Figures 13a to 13d

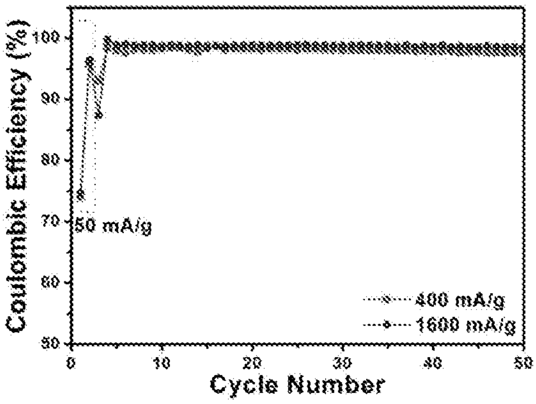


Figure 14

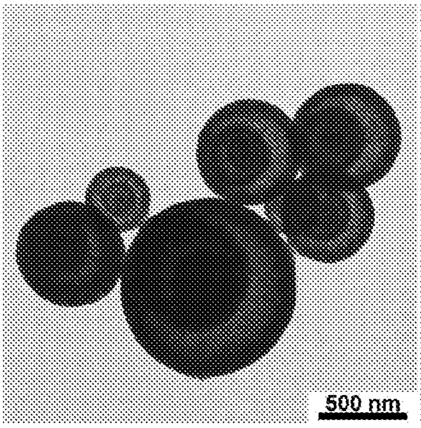


Figure 15a

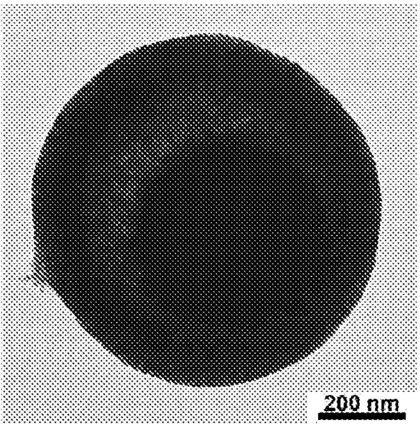


Figure 15b

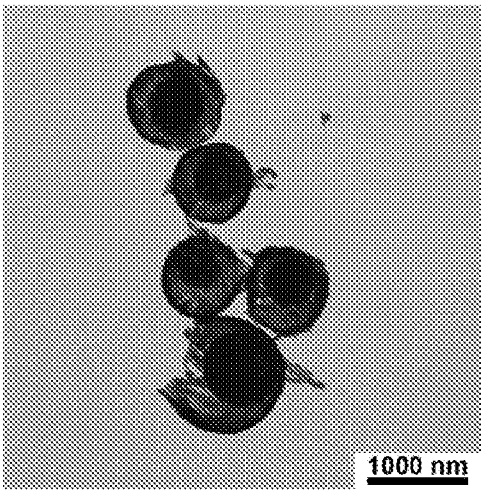


Figure 16a

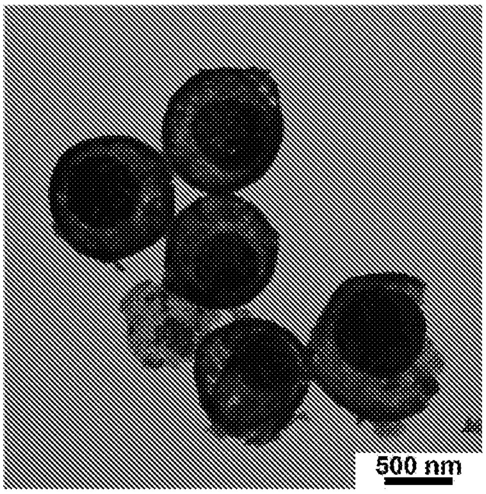


Figure 16b

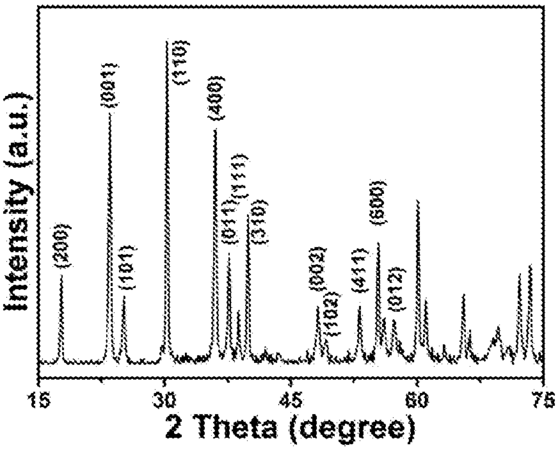


Figure 17

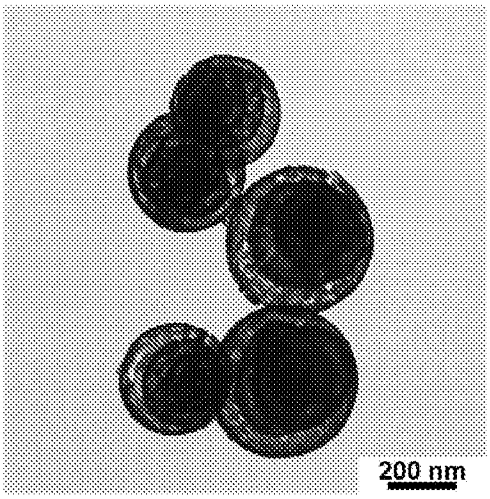


Figure 18

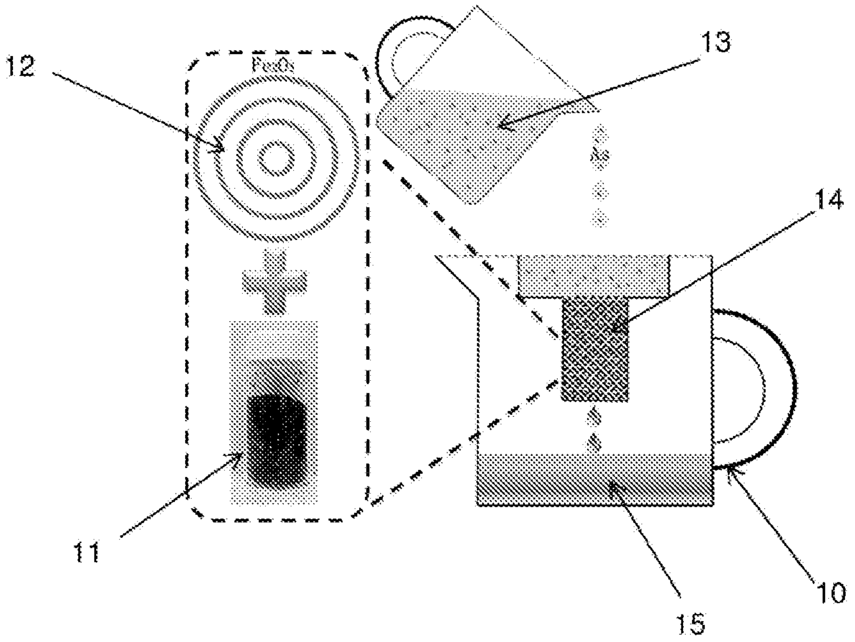


Figure 19

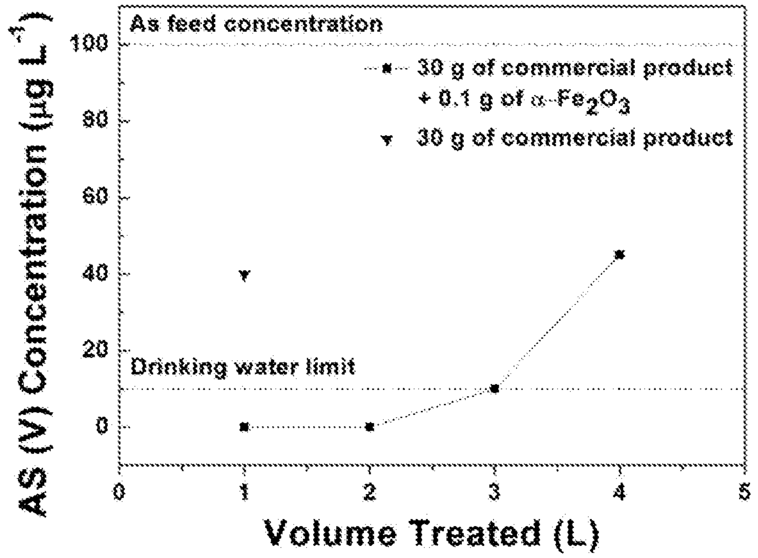


Figure 20

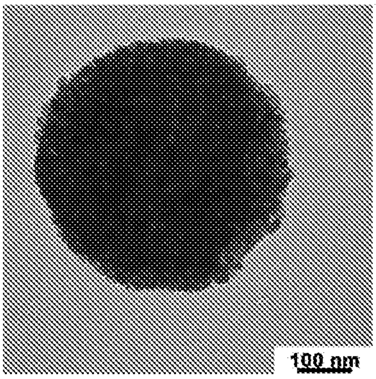


Figure 21a

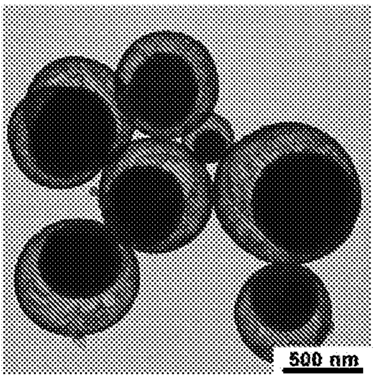


Figure 21b

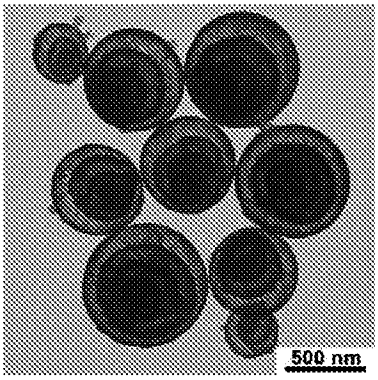


Figure 21c

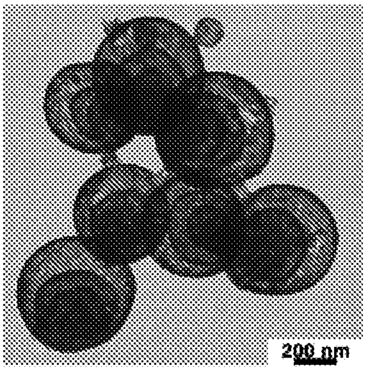


Figure 21d

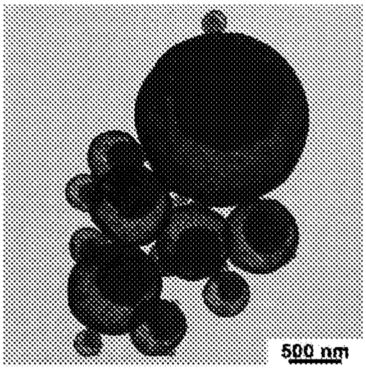


Figure 21e

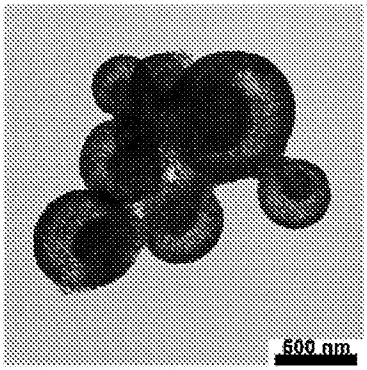


Figure 21f

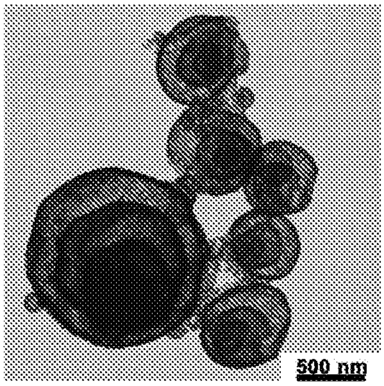


Fig. 21g

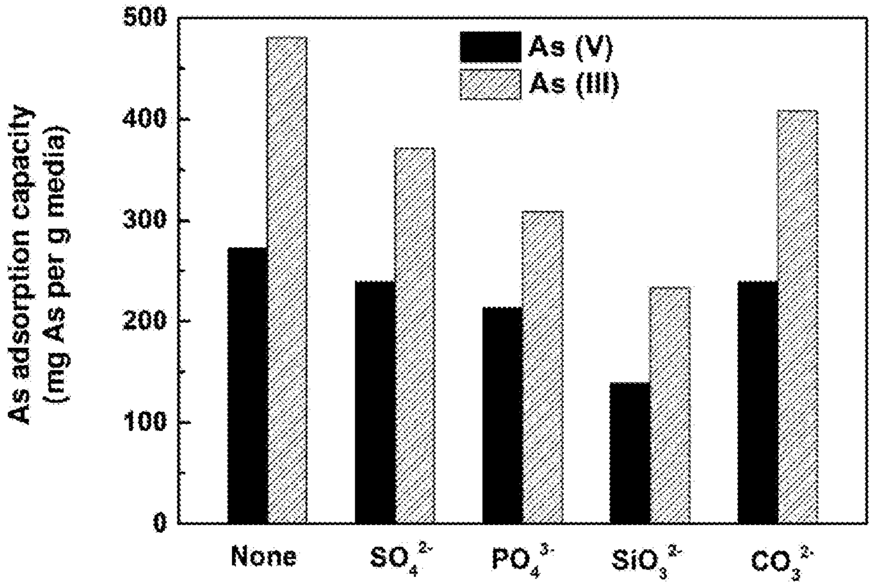


Figure 22

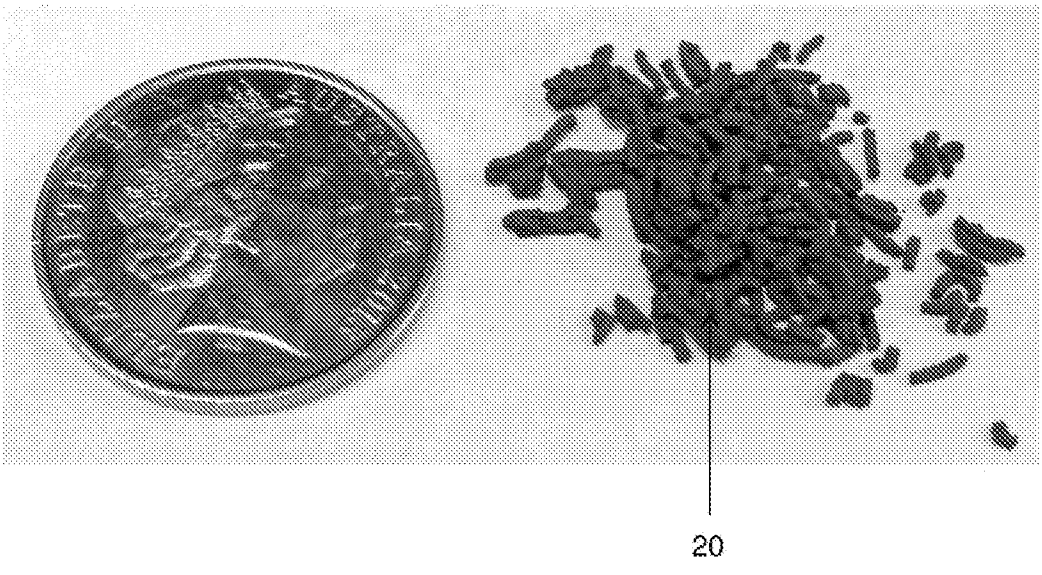


Figure 23

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2014/050038

A. CLASSIFICATION OF SUBJECT MATTER

B01J 13/04 (2006.01) B01J 35/08 (2006.01) H01M 4/1391 (2010.01) C02F 1/28 (2006.01) C07C 5/32 (2006.01)

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)

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)

EPODOC and WPI:/IPC/CPC B01J13/04 or B01J13/20 or B01J20 or H01M4 or C02F1/28 or C07C5/32/LOW or B82Y or B82B or B81C or C08J9/32 and Keywords ((wall 5d multi+), micro+_spheres, spray_drying, metal_oxide, making) & like terms.
EPODOC and WPI: +SHERE+ OR +CAPSULE+ and Keywords (multi-shell+, spray_drying, temperature, organic) & like terms.

Cluster - $PATEN-English full text databases TXTAU1 TXTCA1 TXTEP1 TXTGB1 TXTSG1 TXTUS0 TXTUS1 TXTUS2 TXTUS3 TXTUS4 TXTUS5 TXTWO1 WPI EPODOC and Keyword(s) ((wall 5d multi+), micro+_spheres, spray_drying, metal_oxide, making); (multi-shell+, spray_drying, temperature, organic) & like terms.

GoogleScholar search and keyword(s) (spray drying multi-shelled hollow microspheres; "spray drying" "yolk-shell powder").
AusPat ("yu, chengzhang" IN INV). AusPat ("zhou, liang" IN INV).

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

☒ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents:

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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
29 July 2014	29 July 2014

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
Email address: pct@ipaustralia.gov.au

Authorised officer

John Deuis
AUSTRALIAN PATENT OFFICE
(ISO 9001 Quality Certified Service)
Telephone No. 0262832146

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/0038832 A1 (Gingerich) 26 February 2004 See the abstract; para. [0005]-[0006]; and claims 1-5.	15-17, 19
X	"One-pot facile synthesis of double-shelled SnO_2 yolk-shell-structured powders by continuous process as anode materials for Li-ion batteries"; Hong, Y. J.; Son, M. Y.; Kang, Y. C; Adv. Mater., 2013, 25, 2279–2283; published 01 February 2013. See the Title; and Figures 1 to 3.	15-19, 23, 25
X	"Fabrication and application of inorganic hollow spheres"; Jing Hu, Min Chen, Xiaosheng Fang and Limin Wu; Chem. Soc. Rev., 2011, 40, 5472-5491. See entire document.	15-20, 23, 24, 25, 26-29

International application No.
PCT/AU2014/050038

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:

because they relate to subject matter not required to be searched by this Authority, namely:

the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including

2. ☐ Claims Nos.:

because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos:

because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplemental Box for Details

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Supplemental Box

Continuation of: **Box III**
This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

- Claims 1-14, 21-part A, 22-part A, 23-part A, 24-part A, 25-part A, 26-part A and dependent claims, 30-part A are directed to a method for forming a metal oxide multi-shelled hollow structures comprising the steps of: (i) forming a solution containing at least one dissolved metal compound and at least one organic compound; (ii) spray drying the solution to form composite particles containing at least one metal species and organic material and (iii) heating the composite particles by increasing temperature at a predetermined rate to form the multi-shelled hollow structures. The feature of forming a metal oxide multi-shelled hollow structures, wherein the heating step is carried out by increasing temperature at a predetermined rate is specific to this group of claims.

- Claims 15-20, 21-part B, 22-part B, 23-part B, 24-part B, 25-part B, 26-part B and dependent claims, 30-part B are directed to a multi-shelled hollow structures comprising a metal oxide, the multi-shelled hollow structures comprising at least three hollow shells. The feature of multi-shelled hollow structures comprising at least three hollow shells is specific to this group of claims.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a priori*.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2014/050038**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
US 2004/0038832 A1	26 February 2004	US 6960556 B2	01 Nov 2005
		AU 2003302318 A1	09 Jul 2004
		CA 2496506 A1	01 Jul 2004
		EP 1543095 A2	22 Jun 2005
		IL 166996 A	31 May 2010
		JP 2006508013 A	09 Mar 2006
		KR 20050046736 A	18 May 2005
		KR 100682114 B1	15 Feb 2007
		MX PA05002032 A	19 Oct 2005
		WO 2004055228 A2	01 Jul 2004

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.