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(54) Title: METHOD FOR FORMING MICROSPHERES

(57) Abstract: There is a method for forming microspheres including: obtaining a precursor solution including a template, a carbon precursor, and a surface locking agent dissolved in a solvent; ejecting the precursor solution through a micro-fluidic spray nozzle to form droplets, wherein the droplets are ejected into a drying environment; evaporating at least some of the solvent from the droplets to form microspheres, the microspheres including the template, the carbon precursor or its derivative cross-linked product, and the surface locking agent or its derivative cross-linked product.

Method for forming microspheres

Field of the invention

The present invention relates to a method for the formation of microspheres, such as carbon microspheres and composite microspheres thereof.

Background of the invention

Particulate materials (for example, activated carbon) having micropores are important in modern commercial technologies, for example, as a key component in water purification, gas storage and separation, electrical capacitors, and batteries. The presence of micropores (i.e. pores with a diameter of less than 2 nm) in these materials is advantageous as the micropores provide a huge interface to significantly enhance the capability to host guest molecules for adsorption, catalysis, and other physicochemical reactions. One issue with these materials is that their relatively small pore sizes provide a limitation to molecular diffusion and mass transport, especially where bulk and/or large-sized molecules are involved.

To overcome such limitations, mesoporous materials, such as mesoporous carbon materials, can be used. Mesopores, by virtue of their larger pore size, can encapsulate larger molecules such as large biomolecules, polymers, and nanoclusters. As a result of this, mesoporous materials are regarded as being potentially useful in adsorption and separation processes, energy storage and conversion, and in catalysis. However, one issue that is limiting the adoption of mesoporous materials for use in these situations is that most mesoporous materials, especially mesoporous carbon materials, are in the form of fine powders with irregular shapes, small particle sizes and/or poor size uniformity. Bottlenecks may be encountered when they are applied to dynamic systems, such as dynamic adsorption, chromatography, and fluidized circulating catalysis. To this end, uniform microspheres with large geometrical size are desirable in practice. However, such microspheres are difficult to fabricate, particularly on an industrial scale. Many of the approaches to synthesis of mesoporous materials are lab based and are not readily scalable for industrial production, and it is very difficult to control the size, uniformity, and the mesoporosity of mesoporous microspheres.

There have been a number of attempts to produce mesoporous microspheres using scalable processes, for example, porous microspheres have been fabricated by aerosol

techniques, such as ultrasonic spray pyrolysis and aerosol assisted self-assembly. However, with aerosol techniques, generation of uniform and large droplets from which to form the mesoporous microspheres is difficult; droplets tend to coalesce during formation, or deform upon drying. Another technique that is often employed is a solution-growth technique. However, with solution-growth techniques, growth of uniform microspheres is difficult to achieve and synthesis generally takes too long to produce industrial scale quantities. Furthermore, both of these processes generally produce particles which are too small, have poor size uniformity, and have poor physicochemical properties, including: low surface areas, small pore volumes, disordered and non-uniform pore sizes, and poor pore connectivity and openness - especially at the surface.

The non-uniformity, small particle size, poor physicochemical properties, in the mesoporous microspheres of the prior art, limits their use, especially in an industrial setting where particle performance and integrity is critical, particularly at elevated temperatures and pressures. To this end, uniform mesoporous microspheres with large geometrical sizes and desirable physicochemical properties and a method of producing such microspheres is highly desired.

Accordingly, it is an object of the invention to address at least some of the aforementioned problems.

Reference to any prior art in the specification is not an acknowledgment or suggestion that this prior art forms part of the common general knowledge in any jurisdiction or that this prior art could reasonably be expected to be understood, regarded as relevant, and/or combined with other pieces of prior art by a skilled person in the art.

Summary of the invention

The present invention is directed towards developing a simple yet highly efficient method for fabrication of uniform microspheres, preferably carbonaceous microspheres.

In one aspect of the invention there is provided a method for forming microspheres including: obtaining a spray precursor solution including a template, a carbon precursor, and a surface locking agent dissolved in a solvent; ejecting the spray precursor solution through a micro-fluidic spray nozzle to form droplets, wherein the droplets are ejected into a drying environment; evaporating at least some of the solvent from the droplets to form microspheres,

the microspheres including the template, the carbon precursor or its derivative cross-linked product, and the surface locking agent or its derivative cross-linked product.

The present invention has adopted a microfluidic jet spray drying technology in the preparation of microspheres. The method of the invention provides an integrated molecular assembly method to tune nano-scale textural and structural properties of the microspheres. The use of a micro-fluidic spray nozzle is essential to obtain microspheres with high size uniformity and large geometrical sizes (tunable from several micrometres of a few hundreds of micrometres), both of which cannot be achieved by conventional spray drying technology. Conventional methods generate microspheres with poly-dispersed sizes of sub-micrometres to a few micrometres. The generation of large-sized microspheres is difficult because large spray droplets tend to be easily deformed.

The term template is intended to refer to any inorganic, organic material, or combination of an inorganic and organic material that can be used to form a network structure during formation of the microspheres and without undergoing significant phase separation. In certain embodiments, the template may also play a role in the formation of a mesopore network. The template is, in preferred embodiments, ideally able to be burned off upon pyrolysis or removed by chemical etching to form a mesoporous particle having a mesoporous network. The template is preferably selected from the group consisting of organic molecular blocks that can be thermally decomposed and vaporised upon pyrolysis and/or consisting an inorganic compound that can be dissolved by a common acid (such as hydrochloric acid) or base (such as sodium hydroxide) to generate mesopores. More preferably the template is selected from the group consisting of both hydrophobic and hydrophilic molecular blocks that can form micelle assemblies upon solvent evaporation. These may include: cationic surfactants, such as alkyl-trimethylammonium bromide, anionic surfactants, such as alkyl sulfate, non-ionic surfactants, such as alkyl poly(ethylene oxide) oligomeric surfactants, block copolymers, such as amiphilic poly(ethyleneoxide)-poly(propyleneoxide)- poly(ethyleneoxide) copolymers, and their mixtures thereof. Most preferably the template material is selected from the group of block copolymers consisting of poly(ethyleneoxide) and poly(propyleneoxide) blocks, such as the commercial Pluronic family of block copolymers.

Alternatively, the template may be an inorganic compound such as a metal or semi-metal oxide (such as silica), or a metal or semi-metal salt including salts of alkali metals such as sodium chloride, alkali earth metals, or transition metals.

The term carbon precursor is intended to refer to any organic molecule or polymer that can be used to mitigate deformation of droplets during the drying process to form the microspheres, and in preferred embodiments can be carbonized to carbon microspheres after pyrolysis. Without wishing to be bound by theory, the inventor's believe that as drying proceeds, electrostatic forces within the droplets gradually weaken and the surfaces of the droplets become increasingly elastic due to fast growth of a rigid crust at the surface of the droplets. Capillary forces which drive droplet deformation can overcome the electrostatic forces which stabilise sphericity of the droplet, leading to the formation of a crumpled microsphere particle. The presence of the carbon precursor serves to strengthen the electrostatic forces through hydrogen bonding and to relieve elastic stress through viscous flow, thus preventing or mitigating the formation of crumpled microsphere particles. The carbon precursor can be any organic component as long as it can be polymerized and in preferred embodiments carbonised to carbon after pyrolysis. Preferably the carbon precursor is selected from the group consisting of O- and/or N- containing groups that are capable of forming hydrogen bonds with other carbon precursor molecules, and/or with the template, such as resins, sugars, polymers, and carbohydrates. More preferably the carbon precursor is selected from the group consisting of hydroxyl and/or amino groups, such as phenolic resins, melamine resins, urea resins, aniline resins, their modified counterparts, and their mixtures thereof. Most preferably the carbon precursor is selected from the group of low-molecular-weight phenolic resins, their modified counterparts, and their mixtures with those as mentioned above. The synthesis of low-molecular-weight phenolic resins is known in prior art. An embodiment is illustrated in Example 1.

The term surface locking agent is used to refer to an inorganic or organic constituent that aids in the fast formation of non-sticky (e.g. to prevent coalescence of discrete microspheres) microspheres through the formation of rigid surface crust around the exterior of the droplet as it dries and forms into a microsphere. The surface locking agent also aids in microsphere formation and in certain embodiments can be applied for mesopore generation and/or nanoparticle loading. That is, the surface locking agent may also be the source of an additional porous network or the precursor of nanoparticles. This crust is important for maintaining the morphology and structure of the droplet/microsphere during the drying process and assists in preventing coalescence of the

microsphere particles. The surface locking agent can be any organic or inorganic compound that can preferentially precipitate on the surface of a fast drying droplet to form a surface crust. More preferably the surface locking agent is selected from the group consisting of easily hydrolytic units that are capable of forming hydroxide and/or oxides, such as alkoxides, nitrates, chlorides, and mixtures thereof. Most preferably the surface locking agent is selected from the group consisting of silicon or metal alkoxides (such as Al, Ti, or Zr alkoxides), metal nitrates and chlorides (such as Co, Fe, Ni, Cu, or Mg nitrates or chlorides). Mixtures of different salts may also be used as the surface locking agent.

The solvent used in the present invention can be water or any organic solvent provided that it can well dissolve or mix the above-mentioned molecules or substances. More preferably, the solvent is selected from those can be easily vaporized, such as water and alcohols. Most preferably ethanol or water is used as the solvent.

The use of a micro-fluidic spray nozzle is particularly advantageous as it provides for the formation of droplets which are monodisperse, uniform and large-sized. This in turn promotes the formation of monodisperse, uniform and large-sized microspheres. Unlike in conventional spray drying methods using ultrasonic waves (or other methods) to atomize a liquid to obtain fine droplets with small size and poor size uniformity, the micro-fluidic aerosol nozzle, coupled with a pulse disturbance unit, can afford precise and free control and monitoring of the quality of a droplet, including size, uniformity, and stability.

The micro-fluidic spray nozzle has an orifice diameter of tens to hundreds of micrometres. Preferably the micro-fluidic spray nozzle has an orifice diameter of from about 50 μm to about 150 μm. More preferably, the orifice diameter is from 70 to 120 μm.

In an embodiment, the mass ratios among the template, the carbon precursor, and the surface locking agent in the spray solutions can be freely controlled to obtain carbonaceous microspheres with adjustable morphology, structure, porosity, and functionality. Preferably, the mass ratio of template (x): carbon precursor (y): surface locking agent (z) is $0 \leq x \leq 80$: $1 \leq y \leq 90$: $1 \leq z \leq 70$, wherein $x + y + z = 100$. More preferably, their mass ratio is in the range $20 \leq x \leq 60$: $30 \leq y \leq 60$: $5 \leq z \leq 40$.

In an embodiment, the solute concentration, (i.e. the constituents other than the solvent, which in some embodiments may be determined on the basis of the total amount of the template,

the carbon precursor, and the surface locking agent) can be used to control geometrical sizes, as well as structural and textural properties of the resultant microspheres. Preferably, the solute concentration is from 0.5 wt% to 30 wt%. Most preferably, the solute concentration is from 2 wt% to 20 wt%.

In an embodiment, conventional additives known in the art, such as a crosslinking agent, an acid or a base catalyst to aid the polymerization of the carbon precursor, the hydrolysis and condensation of the surface locking agent, and/or the carbonization of the hybrid microspheres may be added in the spray solution.

In an embodiment, the step of ejecting the precursor solution through the micro-fluidic spray nozzle includes piezoelectrically vibrating the micro-fluidic spray nozzle at a pulse disturbance frequency. Piezoelectrically vibrating the micro-fluidic spray nozzle promotes the formation of monodisperse droplets. Ideally, the monodisperse droplets have a mean diameter that is in the size range of from about 1 μm to about 1000 μm, preferably from about 10 μm to about 500 μm, even more preferably from about 50 μm to about 300 μm, and even more preferably from about 80 μm to about 250 μm, and most preferably about 100 μm to about 200 μm. The term monodisperse as applied to droplets or microparticles is intended to refer to a population of droplets or microparticles that have a coefficient of variation (CV) of up to 5% from the mean (number average) diameter. Preferably the monodisperse droplets have a coefficient of variation of less than 5% from the mean diameter. More preferably, the monodisperse droplets have a coefficient of variation of less than 3% from the mean diameter. Most preferably the monodisperes droplets have a coefficient of variation of less than 2% from the mean diameter.

In an embodiment the number weighted mean diameter of the microspheres formed according to the method of the invention is in the size range of from about 1 μm to about 1000 μm, preferably from about 5 μm to about 500 μm, more preferably from about 10 μm to about 300 μm, and even more preferably from about 15 μm to about 200 μm, and most preferably about 20 μm to about 150 μm. Preferably the microspheres have a coefficient of variation of less than 5% from the mean diameter. More preferably, the microspheres have a coefficient of variation of less than 3% from the mean diameter. Most preferably the microspheres have a coefficient of variation of less than 2% from the mean diameter.

In an embodiment, the pulse disturbance frequency is from about 3 kHz to about 16 kHz. More preferably, the pulse disturbance frequency is from about 6 kHz to about 12 kHz. Most preferably, the pulse disturbance frequency is from about 8 kHz to about 10 kHz. However, more generally a ratio of the normalised pulse disturbance ratio to Reynolds number (ω^*) may be used. This ratio takes into consideration the effect of liquid properties (such as viscosity) disturbance frequency, and flow rate on monodisperse droplet formation. Preferably ω^* is from about 0.2 to about 1.5. More preferably, ω^* is from about 0.3 to 1.3. Most preferably, ω^* is from about 0.45 to 1.15.

In an embodiment the droplets have a droplet radius and a capillary length, wherein the capillary length is greater than the droplet radius. Generally this is important to ensure that the droplets are spherical as they are ejected from the micro-fluidic spray nozzle. The shape of the droplets, as they are formed and ejected, is largely determined by the interplay between capillary and gravitational forces. If the capillary length is larger than the radius of the droplets, the surface tension of the droplets can overcome the effect of gravity and the droplets remain spherical. In an embodiment the capillary length of droplet is in the range of sub- to a few millimetres, while the droplet radius is in the range of tens of to a few hundreds of micrometres.

In an embodiment the drying environment is at a temperature from about 100 °C to about 300 °C. Preferably the temperature is from about 130 °C to about 200 °C. This is advantageous as it promotes rapid drying of the droplets as they are ejected from the micro-fluidic spray nozzle.

In an embodiment, the collected microspheres after the above spray drying may be further subject to a heat treatment at a temperature of from 60°C to 100 °C under static air for a time of from 6 h to 24 h. The purpose of this heat treatment is to ensure a good thermosetting of the carbon precursor (especially when a resin is adopted as the carbon precursor) before carbonization, thus to achieve a possible better yield after carbonization. For the synthesis of the mesoporous carbon microspheres doped with metal or metal oxide nanoparticles, the above heat treatment may be conducted in a closed ammonia atmosphere, the purpose of which is to control the nanoparticle size and dispersion.

In an embodiment the method further includes the step of carbonising carbonaceous material in the microspheres. This process converts at least some of the carbonaceous material

into carbon. Preferably all carbonaceous material is converted to carbon; although it will be appreciated that carbonaceous material may be only partially converted to carbon. The skilled addressee will appreciate that a number of suitable methods may be employed for the carbonization step. However, in a preferred embodiment, the step of carbonising carbonaceous material includes calcining the microspheres in a gas atmosphere, preferably in an inert gas atmosphere. Preferably, the step of calcining the microspheres is conducted at a temperature of from about 300 °C to about 1500 °C. More preferably, the step of calcining the microspheres is conducted at a temperature of from about 600 °C to about 900 °C.

The method may further include the step of removing the surface locking agent from the microspheres to generate mesoporosity. Preferably this step is conducted after carbonising the carbon precursor to carbon. Removal of the surface locking agent provides for mesopores in the carbon microsphere. The skilled addressee will appreciate that a number of suitable methods may be employed for removing the surface locking component from the microsphere. This will in part be dependent on the type of surface locking agent used. However, preferably the removal of the surface locking agent from the microspheres is through chemical dissolution. Certain surface locking agents may be solubilised in aqueous solutions whether acidic or alkali, or in organic solutions. As above, the skilled addressee will be able to determine a suitable solvent for dissolving the inorganic template.

The term mesoporous denotes the presence of mesopores within an object. A mesopore is a term which is well understood in the art to refer to a pore having a pore size (or diameter) of from about 2 nm to about 50 nm. In an embodiment, the mesoporous microspheres have a pore volume of from about 0.1 cm^3/g to about 2.5 cm^3/g. Preferably, the pore volume is from about 0.3 cm^3/g to about 2.0 cm^3/g.

In another embodiment, the method further includes the step of treating the microspheres to form mesoporous carbon microspheres. Preferably the step of treating the microspheres to form mesoporous carbonaceous microspheres includes: carbonising the carbon precursor in the microspheres; and removing the template from the microspheres. The invention thus provides a method for the formation of mesoporous microspheres having ordered mesostructures and mesopores. This is also a significant advance over prior art methods.

In another embodiment, the method further allows the microspheres to be loaded with size-tunable and ultra-dispersed nanoparticles. Nanoparticle loading in a mesoporous material can significantly improve the properties of the microspheres, or provide the microspheres with additional chemical and/or physical properties. Direct loading of nanoparticles with controllable composition, concentration, size, and dispersion, into the microspheres is possible.

One issue that is encountered in prior art systems when attempting to form microspheres doped with nanoparticles, is that the nanoparticles aggregate during loading, adversely affecting the nanoparticle activity and other particle properties, such as the porosity of a mesoporous support. It is relatively difficult to develop a simple, direct, yet efficient method to load uniformly dispersed nanoparticles with desirable size and concentration into a mesoporous material. This difficulty is further exacerbated when the mesoporous material is composed of large microspheres of tens of micrometres. The inventors have advantageously found that including a soluble metal salt into the spray precursor solution and then forming microspheres according to the method of the invention can result in the formation of nanoparticles dispersed within the microspheres.

Thus, in certain embodiments the spray precursor solution further includes a nanoparticle precursor solution, which is generally a soluble metal salt. In this case, after the evaporating step the microspheres additionally include an embedded nanoparticle. This allows the microspheres to be functionalised with a range of metal nanoparticles or ionic nanoparticle compounds. In the situation where the microsphere is subjected to carbonisation (whether by calcination or other method), and subsequent removal of the template (whether by dissolution or other method), a mesoporous carbon microsphere having embedded nanoparticles is formed. By way of example, the method of the invention may be used to produce mesoporous carbon microspheres loaded with ultra-fine super paramagnetic nanoparticles, which are promising for a wide range of applications.

Preferably, the embedded nanoparticles have a diameter of from about 1 nm to about 50 nm. More preferably, the diameter of the embedded nanoparticles is from about 2 nm to about 20 nm.

In another aspect of the invention there is provided a population of monodisperse mesoporous microspheres.

In a further aspect of the invention there is provided a population of monodisperse mesoporous microspheres formed according to the above described method.

The term population is intended to encompass all of the microspheres in a sample or in a production run. Thus the term population may refer to all of the microspheres that are produced in a production process, such as all of the microspheres in a batch, or all of the microspheres that form the output from a continuous production process. The term population is also intended to encompass combined populations of microspheres from multiple batch or continuous synthesis operations, whether the synthesis operations are the same or different.

In an embodiment the number weighted mean of population of microspheres is in the size range of from about 1 μm to about 1000 μm, preferably from about 5 μm to about 500 μm, more preferably from about 15 μm to about 300 μm, and even more preferably from about 20 μm to about 150 μm, and most preferably about 30 μm to about 80 μm. Preferably the population of microspheres has a coefficient of variation of less than 5% from the mean diameter. More preferably, the population of microspheres has a coefficient of variation of less than 3% from the mean diameter. Most preferably the population of microspheres has a coefficient of variation of less than 2% from the mean diameter.

In an embodiment the population of microspheres include a plurality of hollow microspheres. In an alternative embodiment the microspheres are solid. In yet a further embodiment there may be a combination of both hollow and solid microspheres.

In an embodiment the population of microspheres are carbonaceous microspheres.

As used herein, except where the context requires otherwise, the term "comprise" and variations of the term, such as "comprising", "comprises" and "comprised", are not intended to exclude further additives, components, integers or steps.

Further aspects of the present invention and further embodiments of the aspects described in the preceding paragraphs will become apparent from the following description, given by way of example and with reference to the accompanying drawings.

Brief description of the drawings

Figure 1: Illustration of the dynamic "surface locking" mechanism that governs the evolution of morphology, composition and mesostructure during fast drying: (a) the initial droplet, (b) temperature ramp and silica growth at the surface, (c) formation of silica-rich crust that "locks" the droplet, (d) emergence of disordered mesostructure at the interface and hollow cavity inside, (d_1) magnified area at the external surface showing the silica-rich crust and the three component composite micelle assemblies, (d_2) a simple model showing the existence of strong interfacial electrostatic interactions, and (e) shift of the air-liquid interface and growth of both disordered and ordered mesostructures, and hollow cavity.

Figure 2: An SEM image of the carbonised product obtained from the very sticky F127/resol composite collected on a Petri-dish.

Figure 3 An SEM image (a) and a HRSEM image (b) of the crumpled mesoporous silica microparticles.

Figure 4: A schematic illustration showing the configuration of the micro-fluidic jet spray dryer.

Figure 5: A schematic configuration of the nozzle.

Figure 6: Trends of the geometrical particle sizes of the spray dried microspheres and the final mesoporous carbon microspheres as a function of spray drying temperature. The solute content was set at 18 wt%.

Figure 7: Optical images of the just-collected as-dried hybrid composite microspheres obtained at a drying temperature of 160 °C (a), and the corresponding fully thermosetted microspheres (b).

Figure 8: An overall SEM (a), HRSEM (b-h) and TEM (i-k) images of the ordered mesoporous carbon microspheres (a, b, d, and f-j) and the intermediate silica/carbon composite microspheres (c, e, and k) at the external surfaces (b, c), external layers (d, e), middle part (f), inner layer (g) and internal surface (h); insets in (a) are the particle size distribution and half a magnified hollow sphere. The ordered mesoporous carbon microspheres were obtained at 160°C, followed by carbonization at 900°C and silica removal.

Figure 9: SAXS patterns of the hybrid microspheres (a), the carbonized silica/carbon composite microspheres (b, d) and the final ordered mesoporous carbon microspheres after silica removal (c) obtained at a drying temperature of 160 °C.

Figure 10: Elemental analyses of the silica/carbon composite microspheres obtained at a drying temperature of 160 °C at different locations: (a) TGA curves obtained under O_2 flow (45mL/min); showing the overall silica and carbon contents; (b-d) SEM images and EDX spot spectra at the surface, showing the surface elemental components; (e) SEM image of a shell with an arrow along which the elemental scanning profile (f) was obtained and a spot where the elemental components at the cross-section (g) was obtained.

Figure 11: N_2 sorption results of the carbonized silica/carbon composite microspheres obtained at a drying temperature of 160 (a, b) and 170°C (d, e) before (a, d) and after (b, e) crushing, and the final ordered mesoporous carbon microspheres obtained at 160 (c) and 170°C (f).

Figure 12: SEM (a, b, and inset in a) and HRSEM (c-e) images at the external surface (c) and the cross-section (d, e) of the final carbon microspheres obtained at a drying temperature of 170°C.

Figure 13: Trends of the geometrical particle sizes of the spray dried microspheres and the final mesoporous carbon microspheres as a function of solute content. The drying temperature was set at 160 °C.

Figure 14: SEM images of the final mesoporous carbon microspheres obtained at a solute content of 5 (a, b) and 1 wt% (c, d).

Figure 15: HRSEM images of the mesoporous silica/carbon composite microparticles (a, b) and the final carbon microparticles (c, d) with hierarchical mesopores obtained by using a mixture of block copolymer and silica colloids as the template.

Figure 16: SEM (a, b) and TEM (c) images of the mesoporous carbon microspheres with hierarchical pores obtained by using sodium chloride as a template.

Figure 17: SEM images of the hybrid microspheres (a, b) and the final mesoporous carbon microspheres doped with cobalt nanoparticles (c, d). The spray drying temperature was 160 °C.

Figure 18: SAXS pattern (a), N_2 sorption isotherm (b) and the pore size distribution (c) of the mesoporous carbon microspheres doped with cobalt nanoparticles. The spray drying temperature was 160 °C.

Figure 19: TEM images of the mesoporous carbon microspheres doped with cobalt nanoparticles. The spray drying temperature was 160 °C.

Figure 20: SEM (a, b) and TEM (c, d) images of the mesoporous carbon microspheres doped with cobalt nanoparticles. The spray drying temperature was 160 °C. A heat treatment at 60 °C for 3 h under a closed ammonia atmosphere was conducted before carbonization.

Figure 21: SEM (a, c) and TEM (b, d) images of the mesoporous carbon microspheres doped with iron oxide (a, b) and nickel (c, d) nanoparticles. The spray drying temperature was 160 °C.

Figure 22: SEM (a, b) and TEM (c, d) images of the mesoporous carbon microspheres doped with cobalt nanoparticles. The spray drying temperature was 190 °C.

Figure 23: SEM (a) and HRSEM (b) images of the resultant mesoporous silica microspheres after removing the carbon component from the silica/carbon composite microspheres by calcination under static air at 600 °C for 6h. SEM (c, d) images of the mesoporous alumina microspheres.

Figure 24: Evaluation of the dynamic water decontamination performance of the column packing with the ordered mesoporous carbon microspheres obtained from a drying temperature of 160 °C. The insets are the optical images, showing the experimental set-up and a view of the glass column packing with ordered mesoporous carbon microspheres as a substrate.

Detailed description of the embodiments

The present invention provides a versatile method for fabricating uniform mesoporous microspheres, especially carbonaceous microspheres and will be described with reference to preferred embodiments which relate to a method for forming microspheres, and conversion of

the microspheres to mesoporous microspheres, such as mesoporous carbon microspheres. In some embodiments the microspheres or mesoporous microspheres are loaded with nanoparticles.

The method of the present invention allows for microspheres to be produced tunable particle properties, such as microspheres having high uniformity, ordered mesostructures, regular mesopores, high surface areas and porosities, and either solid or hollow architecture, at high production rates. Furthermore, metal or metal oxide nanoparticles with controllable composition, concentration, and nanoparticle size can be directly loaded into the microspheres. Thus, in an embodiment, the microspheres are hollow microspheres. Preferably the hollow microspheres have a shell thickness of from about 5% to about 30% the diameter of the hollow microsphere. More preferably the shell thickness is from about 10% to about 20% of the diameter of the hollow microsphere.

The present invention has adopted a microfluidic jet spray drying technology. This is important for obtaining microspheres with high size uniformity and large geometrical sizes (tunable from several micrometres of a few hundreds of micrometres), both of which cannot be achieved with conventional spray drying technology. Conventional methods only generate microspheres having a poly-disperse size distribution with particles varying in size from tsub-micrometres to a few micrometres. This prior art process is unable to generate large-sized microspheres for a number of reasons, including that large drying droplets tend to be easily deformed.

The present invention demonstrates a general "surface locking" approach to produce monodisperse mesoporous carbonaceous microspheres. In this approach, the colloid chemistry of a droplet suspension is fast driven far from equilibrium such that the surface of the drying droplet can be efficiently locked through formation of a rigid crust. The method enables rapid formation of discrete microspheres from sticky molecular precursors and localization of structure assembly and colloid chemistry inside the locked droplet. Without wishing to be bound by theory, Figure 1 provides an illustration of the detailed formation mechanism of the mesoporous microspheres with a hollow interior during the fast spray drying process.

In the method, a jet of a solution including a template, a carbon precursor, and a surface locking agent is broken up to large and uniform droplets by piezoelectric vibrations through a micro-fluidic nozzle. The droplets are then rapidly dried (within seconds). The drying process

removes a substantial portion of the solvent from the droplets, resulting in the formation of hybrid microspheres that include the template, the carbon precursor (or its partially polymerized derivative), and the cross-linked surface locking agent.

The key to obtain non-sticky microspheres within the short drying time frame lies in: (i) the formation of rich crust of cross-linked surface locking agent which acts against particle coalescence and, (ii) the presence of the a carbon precursor carrying functional groups providing strong electrostatic forces and viscous flows which act to prevent or at least mitigate particle deformation. Without the surface locking agent, the spray-dried microspheres are too soft (or sticky) to collect, leading to particle coalescence and total deformation (Comparative Example 1, Figure 2). Without a carbon precursor acting against droplet deformation, drying droplets deform and crumple, and microspheres cannot be obtained (Comparative Example 2, Figure 3).

The microspheres can then be converted into mesoporous carbonaceous microspheres with a range of desirable physicochemical properties.

Figure 4 shows a set up of a micro-fluidic spray drying apparatus 100 for producing microspheres according to the present invention. The spray drying apparatus 100 includes a drying chamber 102 having an inlet portion 104 and an outlet portion 106.

The inlet portion 104 includes an upper sheet 108 and a perforated lower sheet 110. The upper sheet 108 includes receiving elements 112A and 112B for receiving hot air gun nozzles 114 and micro-fluidic spray nozzles 116 respectively.

The micro-fluidic spray nozzles 116 also include ancillary services such as air pressure lines 118, feed lines 120 for providing feed of a precursor solution to the micro-fluidic spray nozzles 116 from a reservoir of the precursor solution 122 via filters 123, and electrical control lines 124 which control operation of the micro-fluidic spray nozzles 116. In this case, electrical control lines 124 interface with a pulse generator 126 which is computer controlled 128 for controlling piezoelectric elements (not shown) which are part of the micro-fluidic spray nozzles 116. The piezoelectric elements can be controlled to cause the micro-fluidic spray nozzles 116 to vibrate at a pulse disturbance frequency.

The outlet portion 106 includes a sloped region 130, and vibrating motor 132 attached to the sloped region 130, and an outlet 134.

The drying chamber 102 also includes a number of thermocouples (items a, b, c, d, e, and f) to monitor the temperature profile throughout the drying chamber 102.

Figure 5 shows the micro-fluidic spray nozzle 116 in more detail. In this embodiment micro-fluidic spray nozzle 116 includes a tubular body 200, a nozzle holder 202 for mounting the micro-fluidic spray nozzle 116 to the apparatus 100 shown in Figure 4, piezoelectric elements 204 having wires 206 which interface with the electrical control lines 124 of the apparatus 100 of Figure 4, and a capillary outlet 208 having an orifice 210. The micro-fluidic spray nozzle 116 may be fabricated from any material known to be suitable by the person skilled in the art. In this particular embodiment, the micro-fluidic spray nozzle 116 is fabricated from glass.

Figure 5 also shows a view of the micro-fluidic spray nozzle 116 from the front end. In this embodiment the orifice 210 in the capillary outlet 208 has a diameter of 0.01mm. The diameter of the tubular body 200 is 10 mm.

During operation precursor solution is fed from the reservoir 122 to the micro-fluidic spray nozzle 116 through a filter 123 via pressurised air 136. The precursor solution is micronised as it is sprayed through the micro-fluidic spray nozzle 116 into the dryer chamber 102 to form monodisperse droplets of the precursor solution 138. The micro-fluidic spray nozzle 116 is vibrated piezoelectrically through piezoelectric elements 204 at a pulse disturbance frequency that is conducive to the formation of monodisperse droplets of the desired size. The pulse vibrations assist in breaking up the precursor solution into uniform droplets. The pulse disturbance frequency can be controlled and altered via computer 128 which interfaces with pulse generator 126.

The monodisperse droplets 138 in the dryer chamber 102 are subjected to conditions which cause the monodisperse droplets 138 to dry. In this case, the dryer chamber 102 is heated through the use of hot air 140 supplied by hot air guns. The hot air is distributed across the dryer chamber 102 via the perforated lower sheet 110. The temperature of the hot air 140 can be altered such that the rate of drying of the monodisperse droplets 138 can be controlled. In general, as will be discussed, a rapid rate of drying is sought. The drying conditions can be selected such that the monodisperse droplets 138 dry within a couple of seconds. In any event, it

is desirable that the monodisperse droplets 138 have dried before they enter the outlet portion 106 of the dryer chamber 102.

As the monodisperse droplets 138 dry and progress through the dryer chamber 102 they form monodisperse microspheres. These microspheres are collected in the outlet portion 106, in part by the sloped region 130. The vibrating motor 132 is capable of vibrating the sloped region 130 to dislodge any microspheres that may be stuck to the surface of the sloped region 130 and to generally encourage movement of the microspheres on the sloped region 130 to move toward the outlet 134. The microspheres can then be collected from the outlet 134 with suitable collection means, such as a Petri-dish.

As discussed above, for the formation of monodisperse droplets, it has been found that vibrating the micro-fluidic nozzle at a pulse disturbance frequency is important. An analysis of the effect of pulse disturbance frequency on droplet formation has been extensively investigated in the reference: Wu, W. D.; Lin, S. X.; Chen, X. D., Monodisperse Droplet Formation Through a Continuous Jet Break-Up Using Glass Nozzles Operated with Piezoelectric Pulsation. *AICHE J.* **2011,** 57, 1386-1392, the disclosure of this reference is fully incorporated herein.

It was determined that there was a correlation between Reynolds number and the pulse disturbance frequency on the formation of monodisperse droplets. The ratio between actual disturbance frequency (f_{act}) and Reynolds number (Re), denoted as ω, was given as:

$$\omega = \frac{f_{act}}{\mathrm{Re}}$$

The ratio (ω) could be normalised by multiplying the ratio by the characteristic viscous time, giving:

$$\omega^* = \omega \frac{r_j^2}{(\mu/\rho)} = \frac{f_{act}}{(v_j/r_j)}$$

The results indicated that monodisperse droplets would generally form for values of ω^* between 0.47 and 1.12.

According to the present invention, a series of mesoporous carbon microspheres with large geometrical particle sizes can be produced in large quantities. The particle sizes can be

freely tunable from a few micrometres to a few hundreds of micrometres with high monodispersity (CV less than 3 %). This free controllability can be achieved by adjusting one or more of the three factors, namely, the orifice diameter of the microfluidic spray nozzle, the initial solute content of a spray solution, and the drying temperature.

In a set of preferable examples (Examples 1 and 2, Figures 6-14), by using a nozzle with an orifice diameter of 75 μm, by spray drying a solution containing a block copolymer as the template, a phenolic resin as the carbon precursor, and a silicon alkoxide as the surface locking agent, with a solute content of about 20 wt%, the geometrical size of the final resulted mesoporous carbon microspheres can be tuned from about 61 μm to about 81 μm by using a drying temperature from 105 to 180 °C (Examples 1, Figures 6-12). On the other hand, with a drying temperature set at about 160 °C, the geometrical particle size of the resulted carbon microspheres can be more sensitively tuned from about 18 to about 65 μm by adjusting the initial solute from 1 to 18 wt% (Example 2, Figures 13-14).

Also, according to the present invention, carbon microspheres with ordered mesostructures can be obtained by integrating evaporation-induced self-assembly process (structure assembly among a block copolymer, a phenolic resin precursor, and a surface locking agent) into the microfluidic spray drying technology. Furthermore, the type of the ordered mesostructure (such as two-dimensional hexagonal and three dimensional cubic mesostructures) can be tuned by changing the type of the template and/or the mass ratio of the template material and the carbon precursor.

Also, according to the present invention, the mesopore size can be easily controlled by using different templates. Furthermore, hierarchical pores can be also controlled through the use of two different types of templates. In a preferable example (Example 3), the combination of a block copolymer and silica colloid nanoparticles can be used as the template for the synthesis of mesoprous carbon microparticles with hierarchical pores (Figures 15). Yet in another preferable example (Example 4), inorganic salt (such as sodium chloride) can be used as the template for synthesizing carbon microspheres with hierarchical pores (Figures 16).

Also, according to the present invention, the surface area (from a few hundreds to about two thousand square metre per gram) of the carbonaceous microsperes can be freely controlled

by controlling the type and concentration of the template, and/or by controlling the surface locking agent, its type and concentration.

Also, according to the present invention, both solid and hollow mesoporous carbon microspheres can be obtained by controlling the solute content. In a set of preferable examples (Example 1-2), by using a spray nozzle with an orifice of 75 μm, by using block copolymer as a template, phenolic resin as a carbon precursor, and silicon alcoxide as the surface locking agent, mesoporous carbon hollow microspheres can be produced with a solute content of $\geq$ 10 wt%, while solid microspheres can be produced with a solid content of $\leq$ 5 wt%.

Yet as another big advantage of the present invention, ultra-dispersed metal or metal oxide nanoparticles can be directly loaded into the mesoporous carbon microspheres, as detailed below.

According to the present invention, nanoparticles with a wide range of composition, including metals, metal oxides, metal carbides, metal nitrides, and so on, can be loaded into mesoporous carbon microspheres by incorporating a nanoparticle precursor in the spray solution. The conversion of the precursor to the final nanoparticles is associated a carbonization step under a controlled gas atmosphere, preferable nitrogen. In a set of preferable examples (Example 5, Figures 17-21), by using metal nitrates as the nanoparticle precursor, which also serves as the surface locking agent, metal or metal oxide nanoparticles (such as metallic cobalt, iron oxide, and metallic nickel) can be loaded into mesoporous carbon microspheres upon a direct carbonization step.

According to the present invention, another unique aspect and advantage is the capability to control the nanoparticle size by simply controlling the spray drying temperature. In a set of preferable examples (Example 6), the size of cobalt nanoparticles can easily controlled from about 2 nm to about 20 nm by tuning the spray drying temperature from about 190 °C to 160 °C (Figure 22).

Furthermore, according to the present invention, mesoporous metal oxide microspheres can be obtained by removing the carbon component from carbon/metal oxide composite microspheres. In a set of preferable examples (Example 7), by using a block copolymer as the template, phenolic resin as the carbon precursor, an alkoxide as the surface locking agent, after

spray drying and carbonization, mesoporous oxide microspheres can be obtained after removing the carbon component (Figure 23).

The mesoporous carbonaceous microspheres obtained according to the present invention combine a range of desirable physicochemical properties as discussed above. The carbonaceous microspheres can be used in many applications, for example, adsorption and separation, chromotography, catalysis, supercapacitors, batteries, and so on. In a preferbale example, the carbon microspheres can be used for highly efficeint removal of water contamionents under dynamic flowing conditions (Figure 24). The metal-loaded carbon microspheres can be used for a variety of separation and catalytic applications associated with eviromental and energy issures.

Hereafter, the present invention will be described in futher details with reference to a series of examples and drawings. These examples are illustrative only, but the scope of the present invention is not limited thereto.

Examples

Example 1

The carbon precursor (in this case a resol precursor) used was a low-molecular-weight (Mw = 300 ~ 500 g/mol) and soluble phenolic resin. It was prepared from phenol and formaldehyde in a base-catalyzed process. Typically, phenol (8.0 g) was melted at ~45 °C and then stirred with a 20 wt% NaOH aqueous solution (1.68 g) for 10min. Then, a 37-40 wt% formaldehyde aqueous solution (13.76 g) was added below 50°C. Upon further stirring for 1h at ~78 °C, the mixture was cooled to room temperature. The pH value was adjusted to ~7.0 with a 2.0 M HCl solution. Water was removed by rotatory evaporation under vacuum (at ~50mbar) at ~49 °C. Finally, ethanol was added to precipitate NaCl and to dissolve the resols to obtain a 20 wt% solution.

For the synthesis of mesoporous carbon microspheres, a block copolymer Pluronic F127 (12.8 g) was dissolved in a solvent mixture of absolute ethanol (64.0 g) and a 0.2M HCl aqueous solution (8.0 g) at ~40 °C to form a homogeneous solution. Then, tetraethyl orthosilicate (TEOS, 16.64 g) and a 20 wt% of ethanolic resol solution (40.0 g) were added in sequence. The solute content was about 18 wt%. The mixture was stirred for 2 h to allow pre-hydrolysis of TEOS. After this time period, the solution was subject to spray drying experiments. The set-up for the spray drying experiments included a novel micro-fluidic jet spray dryer capable of fast and

continuously producing uniform microparticles in large quantities. A schematic illustration of the dryer is shown in Figure 4. A schematic illustration of the micro-fluidic aerosol nozzle is shown in Figure 5.

For a typical spray drying experiment, the precursor solution prepared as above was stored in a standard stainless steel reservoir and then driven into the micro-fluidic aerosol nozzle with an orifice diameter of ~75 μm by a pressurized air flow. A liquid jet was formed, which was then broken up to a continuous stream of monodisperse microdroplets by pulse disturbance with the aid of periodic piezoceramic vibrations.

The uniformity of the droplets was controlled by applying different pulse frequency and liquid flowing rate and was monitored by a digital SLR camera (Nikon, D90) with a speed light (Nikon SB-400) until a stable and monodisperse droplet jet was formed.

The monodisperse droplets were sprayed into the drying chamber and rapidly dried assisted by the four mounted hot air guns which could produce a heat flow with variable temperatures. Five temperatures (105, 150, 160, 172, 180 °C) were tested, which led to microspheres with different geometrical sizes (Figure 6). The whole drying process was extremely short (typically < 2s). The as-dried microspheres were collected in Petri-dishes at the outlet. As an example, Figure 7A provides an optical image of the collected as-dried hybrid microspheres from a drying temperature of 160 °C.

The collected as-dried microspheres were subject to a heat treatment at 100 °C for 24 h under static air for thermosetting the phenolic resin (this thermal treatment step could be omitted without noticeable influence on the final particle property). As an example, Figure 7B provides an optical image of the fully thermosetted microspheres obtained from a drying temperature of 160 °C. Calcination at 900 °C under a nitrogen flow was conducted, leading to the mesoporous silica/carbon composite microspheres. The silica component in the silica/carbon composite was removed by immersing the microspheres in a 2M NaOH aqueous solution at 50 °C under static conditions for 12 h, followed by another 12 h after changing fresh NaOH solution. Finally, the mixture was filtered off and washed with copious amounts of water and then a small amount of ethanol and the final ordered mesoporous carbon microspheres were dried at ~60 °C overnight.

By using a solute content of about 18 wt% and a nozzle orifice diameter of 75 μm, Figure 6 shows the trends of the geometrical particle sizes of the spray dried hybrid microspheres and

the final mesoporous carbon microspheres as a function of drying temperature, tunable from about 61 μm to 81 μm.

Figure 8A provides the scanning electron microscope (SEM) images of the mesoporous carbon microspheres (after carbonization at 900 °C and silica removal) obtained from a drying temperature of 160 °C. They show uniform spherical morphology with a particle size of ~61.0 μm. Interestingly, they are entirely hollow with a shell thickness of ~9 μm and a cavity diameter of ~43 μm (Figure 8A inset). The mesoporous carbon microspheres possess a highly ordered hexagonal mesostructure (Figure 9). Specifically, four peaks are identified, which are indexed to the 100, 110, 200 and 210 diffractions of a highly ordered hexagonal mesostructure (space group of *p6mm*).

While the overall mesostructure ordering is much higher, there exist ordering gradients in the mesoporous carbon microspheres. High-resolution SEM (HRSEM) images show open and uniform but disordered mesopores at their external surfaces (Figure 8B). Across a carbon shell there is a thin external layer (~500 nm in thickness) with disordered mesopores (Figure 8D). Inwards, highly ordered mesopores are present everywhere (Figure 8F to 8J). Again, without wishing to be bound by theory, the inventors believe that thin silica-rich crusts with a T_g well above room temperature are formed during fast drying, and that this crust can "lock" the surfaces to obtain the microspheres. To verify this assumption, the intermediate silica/carbon composite microspheres were characterized. The external surfaces of the composite microspheres are completely dense without porosity (Figure 8C). Along a typical shell of the composite microspheres there is a dense crust of ~25 nm in thickness (Figure 8E) and a subsequent disordered layer of ~500 nm in thickness (Figure 8E). Inwards, ordered mesopores are present everywhere (Figure 8K). Compositional analyses of the composite microspheres reveal that while the overall silica content is ~56 wt% (Figure 10A), the surface is silica-dominant, >90 wt% (Figure 10B to 10D) and the silica content (59 wt%) (Figure 10E and 10G) at the cross-section is uniform. N_2 sorption isotherms (Figure 11A) of the composite microspheres show a very low adsorption amount. The surface area and pore volume are only ~11 m^2/g and 0.055 cm^3/g. Interestingly, N_2 sorption isotherms of the composite microspheres after crushing show typical type IV curves with a steep condensation step (Figure 11B) with a surface area and pore volume of 327 m^2/g and 0.4 cm^3/g. These results verify the existence of dense silica rich crusts in the composite microspheres.

The carbon microspheres obtained from a drying temperature of 170 °C are spherical and highly monodisperse (Figure 12A and 12B). They are highly uniform of ~68 μm in size, larger than that (~61 μm) of those obtained at 160°C. They are also entirely hollow with a shell thickness of ~7.5 μm and a cavity of ~53 μm. The reason for the improvements in particle sphericity, uniformity and monodispersity, and the increase in particle size, is that the higher drying temperature leads to faster formation of denser and thicker silica crusts. Therefore, the droplet surfaces can be locked and the sizes can be frozen much earlier and more efficiently during spray drying. The carbon microspheres also show open mesopores at the surface (Figure 12C). The shell is composed of a disordered and ordered layer of ~4.7 and ~2.8 μm, respectively (Figure 12D and 12E).

N_2 sorption isotherms of the mesoporous carbon microspheres obtained at a drying temperature of 160°C demonstrate type IV curves with two condensation steps (Figure 11C). The surface area and total pore volume are as high as ~1930 m^2/g and 1.62 cm^3/g. The pore sizes are very narrow, centred at ~2.0 and ~5.5 nm. The porosity of the ordered mesoporous carbon microspheres is up to ~90% and the bulk density is only ~0.191 g/cm^3, while the "true" density is ~2.15 g/cm^3. The surface areas and pore volumes of the final mesoporus carbon microspheres obtained at a drying temperature of from 105 to 180 °C are all similar (Figure 11D to 11F).

Example 2

All the synthetic parameters were the same as those described in Example 1, except that the drying temperature was set at 160 °C, while the solute content was varied between 1 wt% and 18 wt%. This was to show the capability to easily control the geometrical size of the final mesoporous carbon microspheres.

Figure 13 provides the trends of the geometrical sizes of the spray dried hybrid microspheres and the final resulted mesoporous carbon microspheres as a function of solute content. By using a spray nozzle with an orifice diameter of 75 μm, the geometrical size the carbon microspheres can be controlled from about 18 to 65 μm by using a solute content of 1 wt% to 18 wt%.

Figures 14 provide the SEM images of the typical carbon microspheres obtained from a solute content of 5 wt% and 1 wt% both at drying temperature of 160 °C. These carbon microspheres have very uniform geometrical sizes. They all have ordered two-dimensional

hexagonal mesostrusure, similar surface areas (around 1800 m^2/g), pore sizes (around 2.2 and 5.6 nm), and pore volumes (around 1.5 cm^3/g).

At a solute content of ≤ 5 wt%, the mesoporous carbon microspheres were solid (Figures 14), while those obtained at a solute content of ≥ 10 wt% are hollow (Figure 8).

Example 3

As an example for the synthesis of mesoporous carbon microspheres with hierarchical mesopores, a silica colloid (20.0 g of 15 wt% Ludox silica nanoparticles with a particle size of 12 nm) was added into 10.0 g of 20 wt% of the resol precursor under vigorous stirring. Then a blok copolymer Pluronic F127 (2.0 g) was dissolved in water (48 g) and was added into the above mixture slowly under vigorous stirring. The spray solution was further stirred for 30 min and then subject to spray drying by using a spray nozzle with an orifice diameter of 75 μm. The drying temperature was set at 168 °C, while the other treatment steps were the same as those described in Example 1, leading to the carbon microparticles with hierarchical mesopores.

SEM images of the carbonised composites microspheres before removing the silica colloid nanoparticles show mesopores of about 6-10 nm along with packed silica colloid nanoparticles (Figure 15A, 15B). SEM images of the microspheres after removing the silica colloid nanoparticles show an additional uniform mesopore network of about 12 nm in size due to removal of the silica colloids (Figure 15C, 15D).

Example 4

As an example for the synthesis of hierarchical porous carbon microspheres with a salt as the template, sucrose (5.0 g) was dissolved in a mixture formed from 64 g of water and 0.56 g of concentrated sulphuric acid. Then, 2.0 g of sodium chloride was added and stirred until fully dissolved. This solution was then subject to spray drying by using a spray nozzle with an orifice diameter of 75 μm. The drying temperature was set at 175 °C, while the other treatment steps were the same as those described in Example 1, leading to the carbon microspheres with hierarchical pores.

Figure 16 shows SEM and TEM image of the carbon microspheres with hierarchical pores, including uniform mesopores of 5 ~ 10 nm, and macropores of a few hundreds of

nanometres. The microspheres have highly uniform particle size of about 65 μm, and have highly open surface. The surface area is about 400 m^2/g and the pore volume is about 0.20 cm^3/g.

Example 5

For the synthesis of mesoporous carbon microspheres doped with ultra-dispersed metal or metal oxide nanoparticles, a metal salt can serve as a surface locking agent and a precursor for the metal or metal oxide nanoparticles at the same time. As a most preferable example, a block copolymer Pluronic F127 (5.0 g) was dissolved in ethanol (70.0 g) to form a clear solution. Then a 20 wt% ethanolic solution of the resol precursor (25.0 g) was added under stirring. Then, a cobalt nitrate (1.0 g) was added. After stirring for 10 min, a clear solution was obtained, which was then subject to spray drying experiment. Typically, a spray nozzle with an orifice diameter of 75 μm was adopted. All the spray drying and treatment steps and conditions were the same as those described in Example 1, except that the spray drying temperature was set at 160 °C, the temperature for carbonization was 600 °C and the dwell time was 3 h. During the carbonization step, the resol precursor was canbonized to carbon, the block copolymer was removed to generate the mesopore network, while the cobalt nitrate was decomposed and reduced to metal nanoparticles.

Figure 17 provides the SEM images of the as-collected hybrid microspheres and the final mesoporous carbon microspheres doped with cobalt nanoparticles. They are very uniform of 57.5 and 45.3 μm, respectively. The microspheres have highly ordered two-dimensional hexagonal mesopres (Figure 18A) with a uniform pore size of about 5.0 nm (Figure 18C). The surface area and pore volume are about 760 m^2/g and 0.65 cm^3/g (Figure 18B). The cobalt nitrate was converted to metallic cobalt after carbonization. The cobalt nanoparticle size is uniform of about 10-25 nm (Figure 19). The mass content of metallic cobalt nanoparticles in the microspheres is about 12 wt%. These carbon microspheres with cobalt nanoparticles have highly strong magnetic strength (super-paramagnetic behaviour).

As discussed before, the heat treatment of the as-collected hybrid microspheres after spray drying might be carried in an appropriate atmosphere. In this example, the collected hybrid microspheres can be subject to a heat treatment under a closed ammonia atmosphere at 60 °C for 3 h, followed by the same procedure for carbonization. Such a treatment leads to cobalt

nanoparticles with much smaller nanoparticle sizes (3-5 nm) and more uniform dispersion in the mesoporous carbon microspheres (Figure 20).

Also, it is to be advised that, similar to the cases for the synthesis of mesoprous carbon microspheres without nanoparticle loading as descried in Examples 1 to 4, for the mesoporous carbon microspheres loaded with nanoparticles, the geometrical particle sizes can be also freely controlled from several to a few hundreds of micrometres by tuning the orifice diameter of the spray drying nozzle, the spray drying temperature and more sensitive, the solute content; the mesopore structure, surface area, pore size and porosity, and either hollow or solid microspheres can be all freely controlled by changing either a single or more parameters including but not limited to the type of template, carbon precursor, and surface locking agent, their mass ratio.

Also, the concentration of the metal nanoparticles loaded in the final mesoporous carbon microspheres can be controlled over a wide range (preferably from 2 wt% to 50 wt%) by simply changing the mass ratio between the metal salt and the resol precursor.

Last but not least, the composition of the nanoparticles loaded in the mesoporus carbon microspheres can be freely controlled by simply changing the type of metal precursor or combining two or more precursors. For sample, metal (such as iron, nickel, copper, zinc, magnesium, and calcium) nitrates and chlorides can be all adopted as the nanoparticle precursor for synthesizing mesoporous carbon microspheres loaded with nanoparticles with different compositions. For example, Figure 21 provides the SEM and TEM images of the mesoporous carbon microspheres loaded with iron oxide and nickel nanoparticles.

Example 6

As mentioned before, one of the distinguish advantage in the present invention for nanoparticle loading is the capability to simply yet highly efficiently control the nanoparticle size by changing the spray drying temperature. As a preferable examples, the same spray solution as described in Example 5 was prepared and was then subject to spray drying experiment. All the spray drying and treatment steps and conditions were the same as those described in Example 5, except that the spray drying temperature was 190 °C. After spray drying, the collected hybrid microspheres were directly subject to carbonization at 600 °C for 3 h.

Figures 22 provides the SEM and TEM images of the uniform mesoporous carbon microspheres loaded with cobalt nanoparticles obtained at a spray drying temperature of 190 °C. The TEM images show significant differences in nanoparticle size and dispersion in these microspheres as compared to those obtained at a drying temperature of 160 °C (Figure 19). It was amazing that ultra-fine and ultra-dispersed cobalt nanoparticles with controllable sizes from about 2 to 20 nm can be easily loaded into mesoporous carbon microspheres simply by changing spray drying temperature.

Example 7

The surface locking approach can be adopted for synthesizing other mesoporous microspheres that are hardly approachable by other methods. For example, mesoporous silica and alumina microspheres can be fabricated. As a preferable example, a block copolymer Pluronic F127 (3.2 g) was dissolved in ethanol (16.0 g) to form a clear solution. Then a 20 wt% ethanolic solution of the resol precursor (16.0 g) was added under stirring. Then, an aluminium nitrate (0.5 g) was added. After stirring for 1 h, the clear solution was subject to spray drying experiment. Typically, a spray nozzle with an orifice diameter of 75 μm was adopted. The spray drying temperature was set at 160 °C. The collected microspheres were first carbonized at 600 °C for 3 h to get the alumina/carbon composite microspheres. Finally, the carbon component was burned off by calcination at 600 °C for 5 h under static air, leading to the mesoporous alumina microspheres. Figure 25 provides the SEM images of the alumina microspheres.

Example 8

As a proof-of concept, the mesoporous carbon microspheres can be highly efficiently packed in a column for dynamic water treatment with low pressure drop and superior performance.

The dynamic adsorption unit consisted of a glass cylindrical column with a length of ~4.5 cm and an inner diameter of 0.64 cm. To fully fill the volume of the column, ~0.28 g of the mesoporous carbon microspheres was required. For the dynamic adsorption test, a highly concentrated dye (basic red 9) solution (100 mg/L) was stored in the plastic reservoir which was connected with the column through pipelines. The solution was passed through the column. The concentration of the eluted solution after passing through the column was continuously measured to test the performance for dynamic water decontamination.

The pressure drop across the glass column (inset in Figure 24) is quite low. Without applying any external pressure, a flow rate of ~0.8 mL/min (the corresponding flux is ~1500 $L/m^2/h$) can pass through the column. By applying a small external pressure of ~100 kPa, a flow rate of ~2.0 mL/min (the flux is ~3750 $L/m^2/h$) can be achieved. It is found that highly concentrated (100 ppm) dye molecules can be fast removed with pure water produced. The cumulative uptake capacity is ~45 mg/g when pure water can be produced at a flow rate of 2.0 mL/min, while the capacity (~180 mg/g) is still far under saturation after ~450 mL of the dye solution is passed through (Figure 24). The results clearly indicate the promising potential of these mesoporous carbon microspheres.

Comparative Example 1

To study the role of a surface locking agent, a spray solution without the addition of this agent was prepared. As a preferable example, a block copolymer Pluronic F127 (6.4 g) was dissolved in a mixture of absolute ethanol (28.7 g) and a 0.2M HCl aqueous solution (4.0 g), followed by the addition of a 20 wt% ethanolic resol solution (32.0 g). The solid content was set at ~18 wt%. The mixture was stirred at ~40 °C for 2h. The solutions were immediately used for spray drying experiments at 200 °C. The collected soft particles were stuck together, which were then subject the same heat treatment as that described in Example 1.

In this case, microspheres cannot be formed. Without wishing to be bound by theory, the inventors believe that the reason for this lies in the low glass transition temperature (Tg). The template F127 has a Tg of ~-64°C, while the Tg of resols is even lower. Thermosetting of resols is limited in 2s, although the temperature is up to 200 °C. Therefore, the collected F127/resol composite still has a very low Tg such that they can easily deform and stick together. Only with resols highly cross-linked to solid phenolics, can non-sticky polymer microspheres be obtained, which is extremely difficult to achieve within 2s. Figure 2 provides a SEM image of the corresponding mesoporous carbon particles.

Comparative Example 2

To study the role of the carbon precursor for forming microspheres, a spray solution without the addition of a carbon precursor was prepared. As a preferable example, Pluronic F127 (6.4 g) was dissolved in a solvent mixture of absolute ethanol (30.8 g) and a 0.2 M HCl aqueous solution (6.4 g), followed by the addition of TEOS (13.3 g). The solid content was set at ~18

wt%. The mixture was stirred at ~40 °C for 2h. The solutions were immediately used for spray drying experiments at 160 °C. The collected microparticles were then subject a heat treatment at 100 °C under static air for 24 h, and then calcination under air at 550 °C for 5 h.

It was found that dramatic droplet deformation occurred during fast drying, leading to significantly crumpled mesoporous silica microparticles (Figure 3).

It will be understood that the invention disclosed and defined in this specification extends to all alternative combinations of two or more of the individual features mentioned or evident from the text or drawings. All of these different combinations constitute various alternative aspects of the invention.

CLAIMS

1. A method for forming microspheres including:

obtaining a precursor solution including a template, a carbon precursor, and a surface locking agent dissolved in a solvent;

ejecting the precursor solution through a micro-fluidic spray nozzle to form droplets, wherein the droplets are ejected into a drying environment;

evaporating at least some of the solvent from the droplets to form microspheres, the microspheres including the template, the carbon precursor or its derivative cross-linked product, and the surface locking agent or its derivative cross-linked product.

2. The method of claim 1 wherein the step of ejecting the precursor solution through the micro-fluidic spray nozzle includes piezoelectrically vibrating the micro-fluidic spray nozzle at a pulse disturbance frequency.

3. The method of claim 2, wherein the pulse disturbance frequency is from about 3 kHz to about 16 kHz.

4. The method of claim 2 wherein the pulse disturbance frequency and a Reynolds number of the solution are at a normalised ratio (ω^*) of from about 0.2 to about 1.5.

5. The method of claim 4 wherein ω^* is from about 0.45 to about 1.15

6. The method of any one of the preceding claims, wherein the micro-fluidic spray nozzle has an orifice diameter of from about 10μm to about 150 μm.

7. The method of any one of the preceding claims, wherein the droplets are monodisperse in size.

8. The method of any one of the preceding claims, wherein the droplets have a radius and a capillary length, wherein the capillary length is greater than the radius.

9. The method of any one of the preceding claims, wherein the drying environment is at a temperature from about 100°C to about 300°C.

10. The method of any one of the preceding claims, wherein the template is an organic polymer, an inorganic compound or a mixture thereof.

11. The method of any one of the preceding claims, wherein the template is an organic template selected from the group consisting of cationic surfactants, anionic surfactants, and non-ionic surfactants, or mixtures thereof.

12. The method of any one of claims 1 to 10, wherein the template is an inorganic template selected from the group consisting of a metal or semi-metal oxide, a metal or semi-metal salt.

13. The method of any one of the preceding claims, wherein the carbon precursor is selected from the group consisting of phenolic resins, melamine resins, urea resins, aniline resins, their modified counterparts, sugars, polymers, and carbohydrates, and mixtures thereof.

14. The method of any one of the preceding claims, wherein the surface locking agent is selected from the group consisting of silicon or metal alkoxides, metal nitrates, metal chlorides, and mixtures thereof.

15. The method of any one of the preceding claims, further including the step of carbonising carbonaceous material in the microspheres.

16. The method of claim 15, wherein the step of carbonising carbonaceous material includes calcining the microspheres.

17. The method of claim 16, wherein step of calcining the microspheres is conducted at a temperature of from about 300°C to about 1500°C.

18. The method of any one of the preceding claims, further including the step of removing the surface locking agent from the microspheres to form a mesoporous microsphere.

19. The method of claim 18, wherein the step of removing the surface locking agent from the microspheres is through dissolving the surface locking agent from the microspheres.

20. The method of any one of claims 1 to 14, further including the step of treating the microspheres to form mesoporous microspheres.

21. The method of claim 20, wherein the step of treating the microspheres to form mesoporous carbonaceous microspheres includes:

carbonising carbonaceous material in the microspheres; and

removing the inorganic template from the microspheres.

22. The method of any one of the preceding claims wherein the spray precursor solution further includes a nanoparticle precursor selected from the group consisting of a soluble metal or semi-metal salt, such that after the evaporating step the microspheres additionally include embedded nanoparticles.

23. The method of any one of the preceding claims wherein the spray precursor solution has a mass ratio of template (x): carbon precursor (y): surface locking agent (z) such that $0 \leq x \leq 80$: $1 \leq y \leq 90$: $1 \leq z \leq 70$, and $x + y + z = 100$.

24. The method of claim 23, wherein the mass ratio is $20 \leq x \leq 60$: $30 \leq y \leq 60$: $5 \leq z \leq 40$.

25. The method of any one of the preceding claims, wherein microspheres have a number weighted mean diameter of from about 1 μm to about 1000 μm.

26. The method of claim 25, wherein the number weighted mean diameter is from about 20 μm to about 150 μm.

27. The method of any one of the preceding claims wherein the microspheres are hollow microspheres.

28. The method of claim 27 wherein the hollow microspheres have a shell thickness of from about 5% to about 30% the diameter of the hollow microsphere.

29. The method of any one of claims 1 to 26, wherein the microspheres are solid microspheres.

30. The method of any one of the preceding claims wherein the spray precursor solution includes a solute portion, the solute portion including all of the constituents of the spray precursor solution other than the solvent, wherein the solute concentration is from about 0.5 wt% to about 30 wt% of the spray precursor solution.

31. The method of claim 30, wherein the solute concentration is from about 2 wt% to about 20 wt%.

32. The method of claim 18 or 20, wherein the mesoporous microspheres have a pore volume of from about 0.3 cm^3/g to about 2.5 cm^3/g.

33. The method of claim 32 wherein the pore volume is from about 0.3 cm^3/g to about 2.0 cm^3/g.

34. The method of claim 22, wherein the embedded nanoparticles have a diameter of from about 1 nm to about 50 nm.

35. The method of claim 34, wherein the diameter of the embedded nanoparticles is from about 2 nm to about 20 nm.

36. A population of monodisperse mesoporous microspheres.

Figure 1

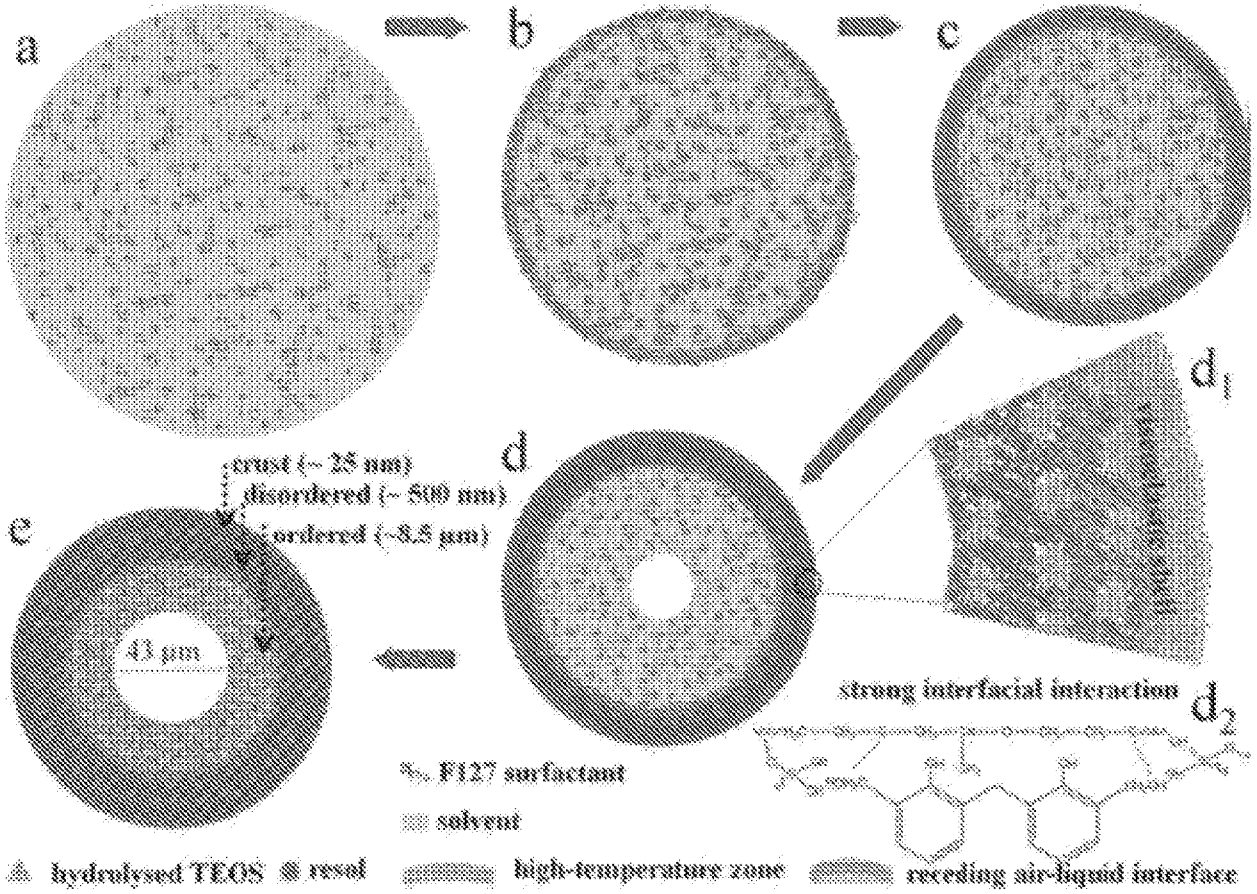

a
b
c
d
d1
d2
e
crust (~ 25 nm)
disordered (~ 500 nm)
ordered (~8.5 μm)
43 μm
strong interfacial interaction
F127 surfactant
solvent
hydrolysed TEOS
resol
high-temperature zone
receding air-liquid interface

Figure 2

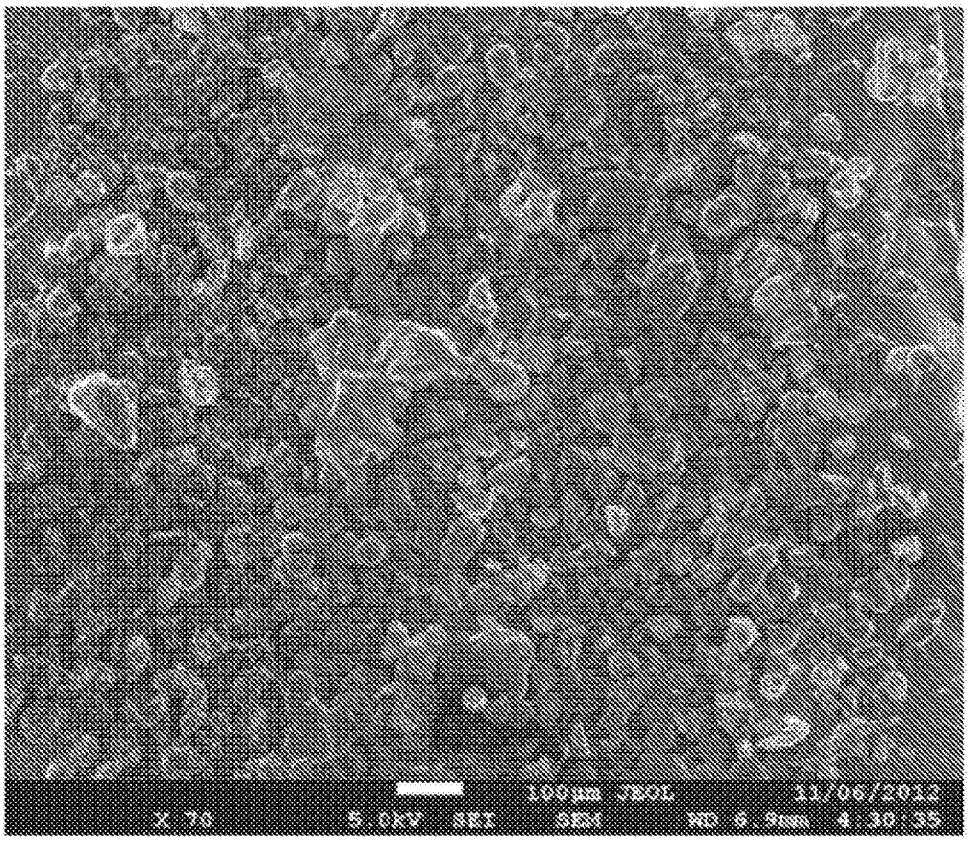


Figure 3

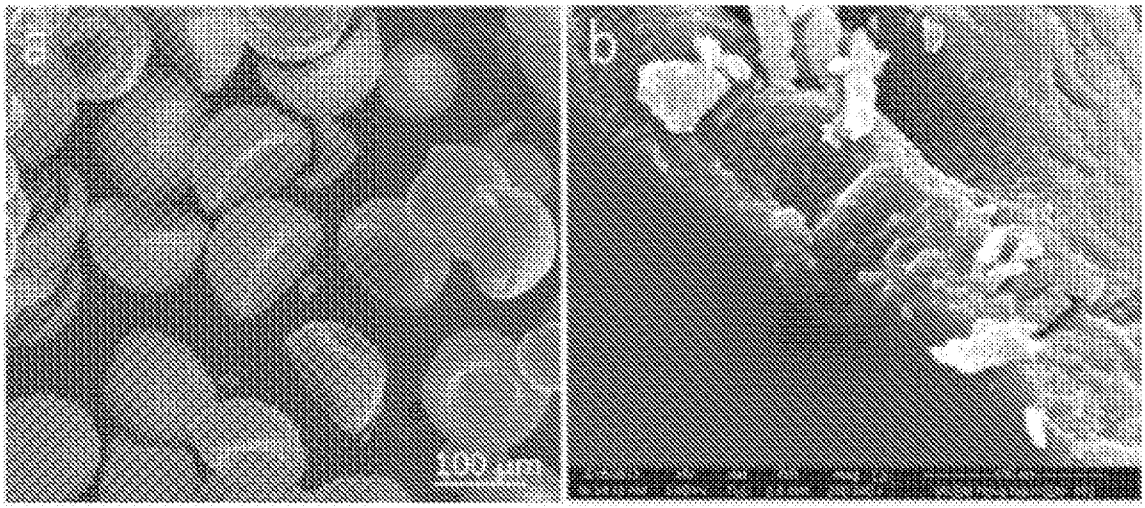


Figure 4

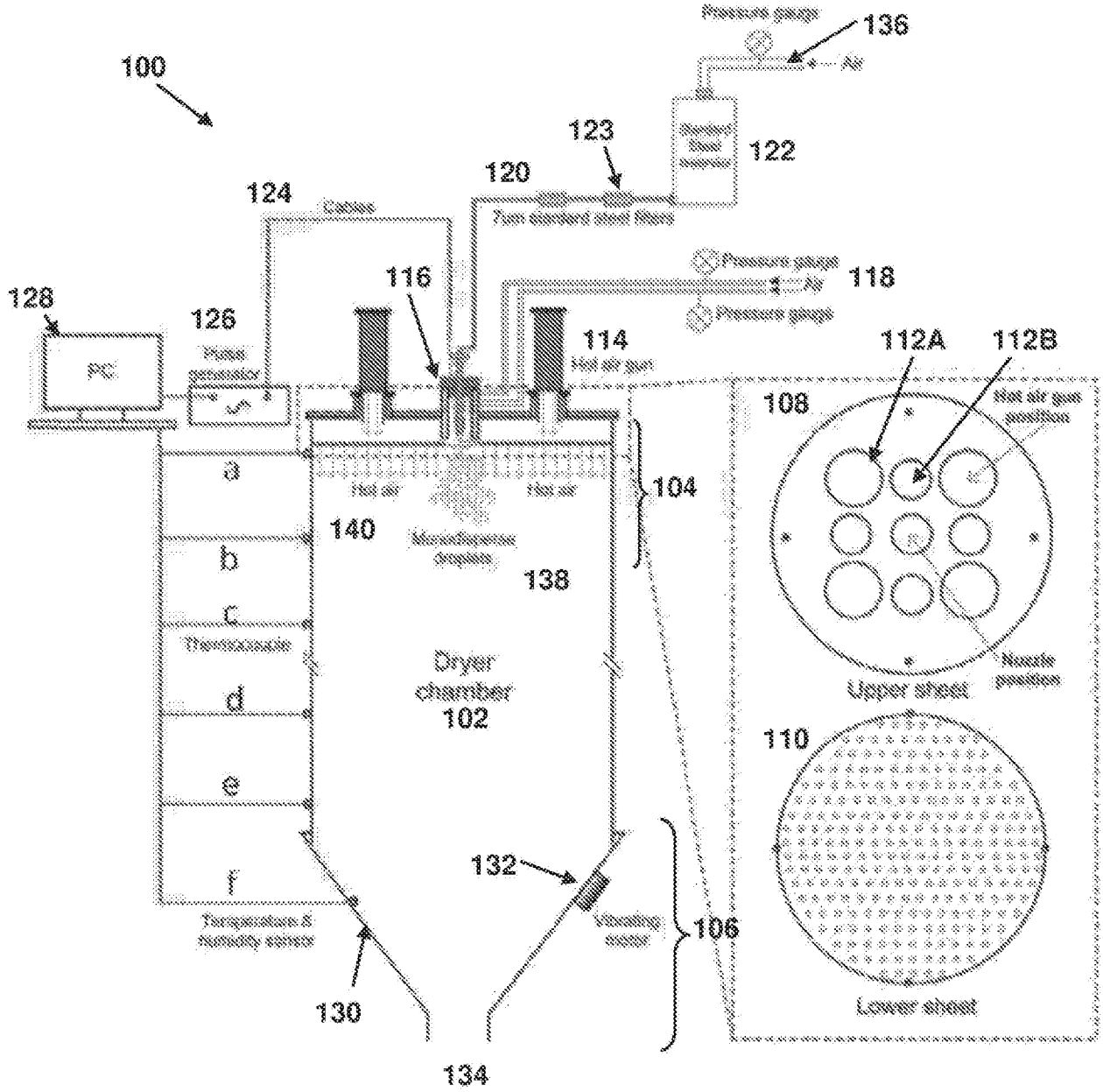

100
136
123
122
120
124
116
118
128
126
114
112A
112B
108
104
a
b
c
d
e
f
140
138
Dryer chamber 102
110
132
106
130
134
Upper sheet
Lower sheet

Figure 5

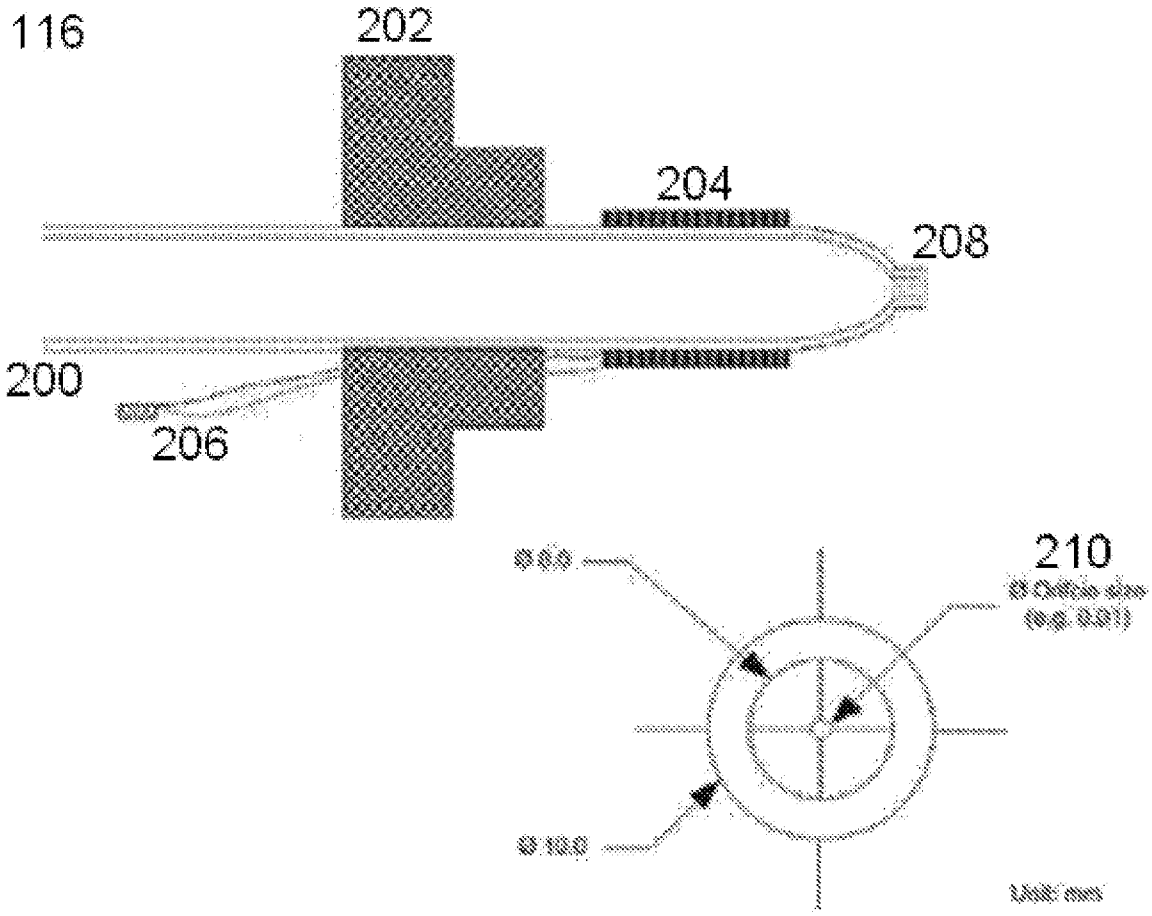


Figure 6

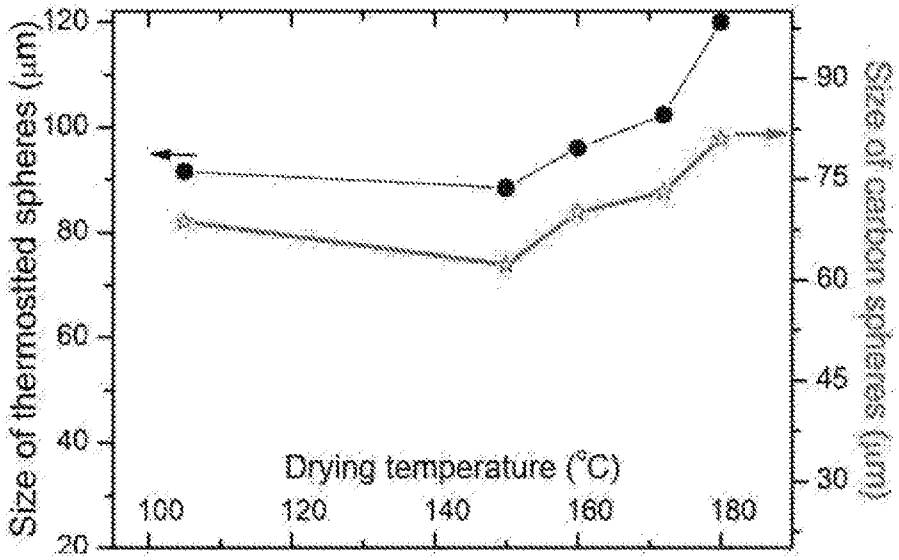

Size of thermosted spheres (μm)
120
100
80
60
40
20
Drying temperature (°C)
100
120
140
160
180
Size of carbon spheres (μm)
90
75
60
45
30

Figure 7

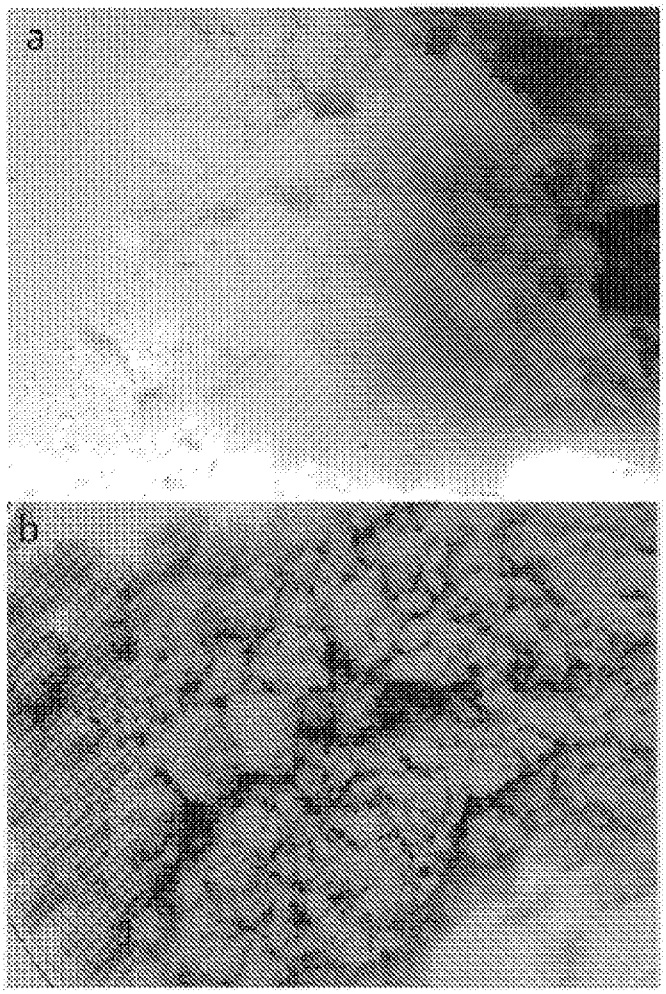


Figure 8

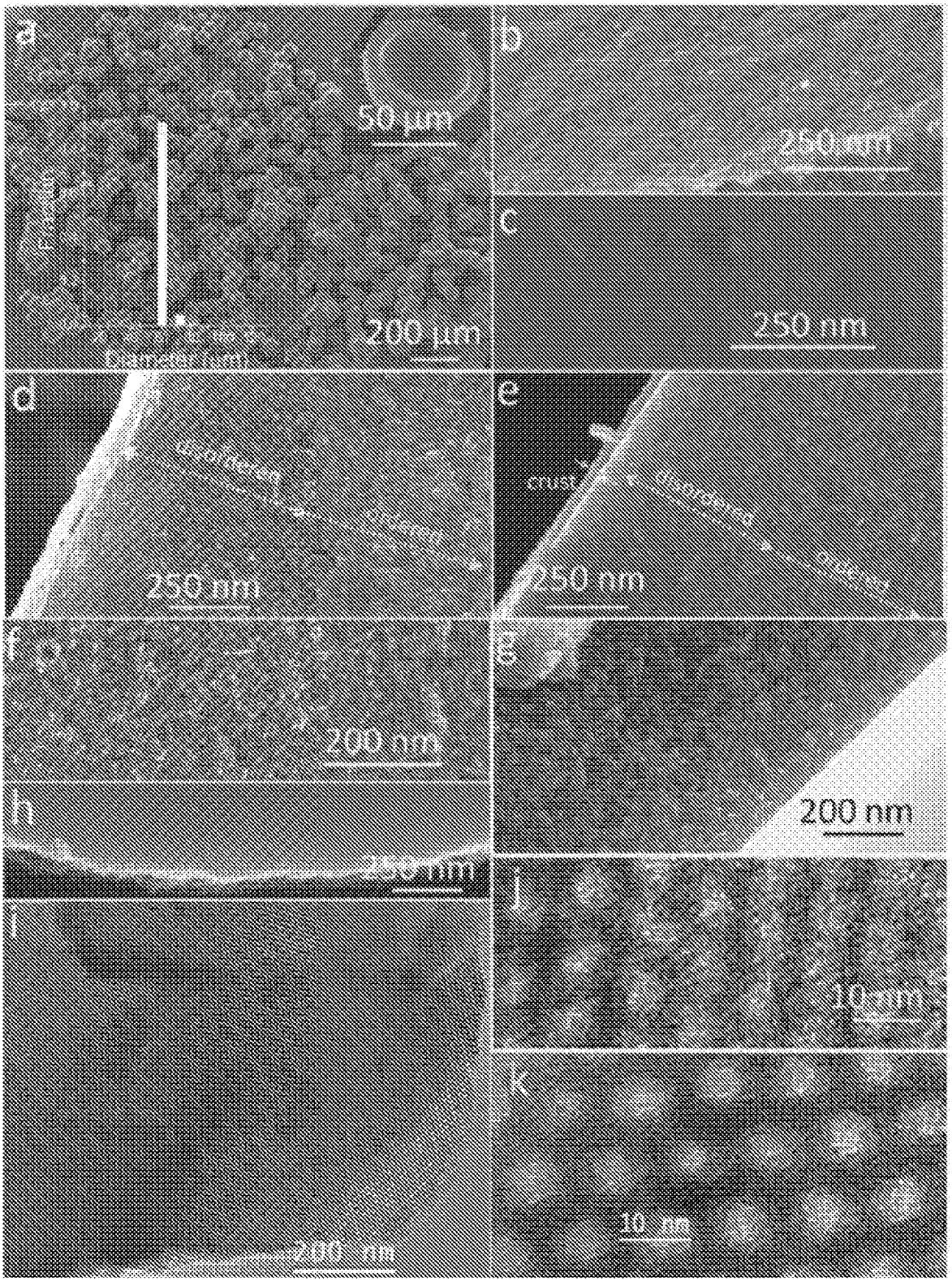

a
50 µm
200 µm
b
250 nm
c
250 nm
d
250 nm
e
250 nm
f
200 nm
g
200 nm
h
i
200 nm
j
10 nm
k
10 nm

Figure 9

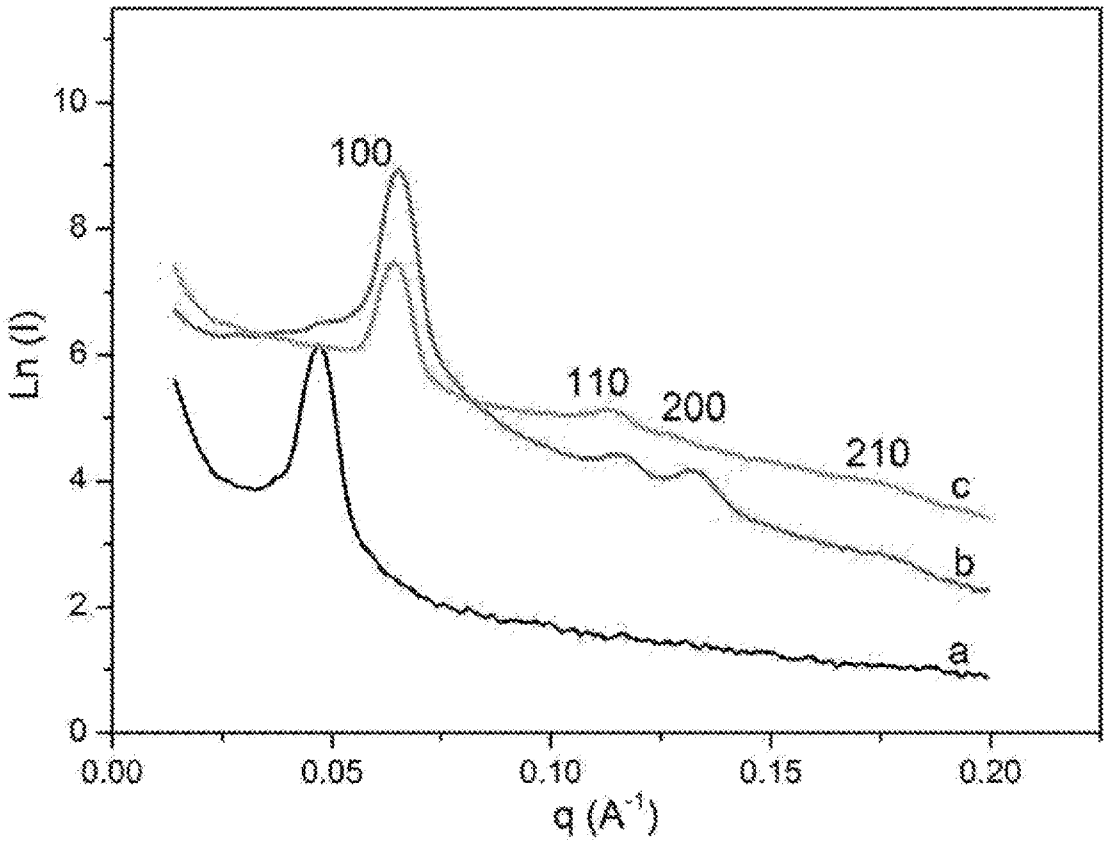


Figure 10

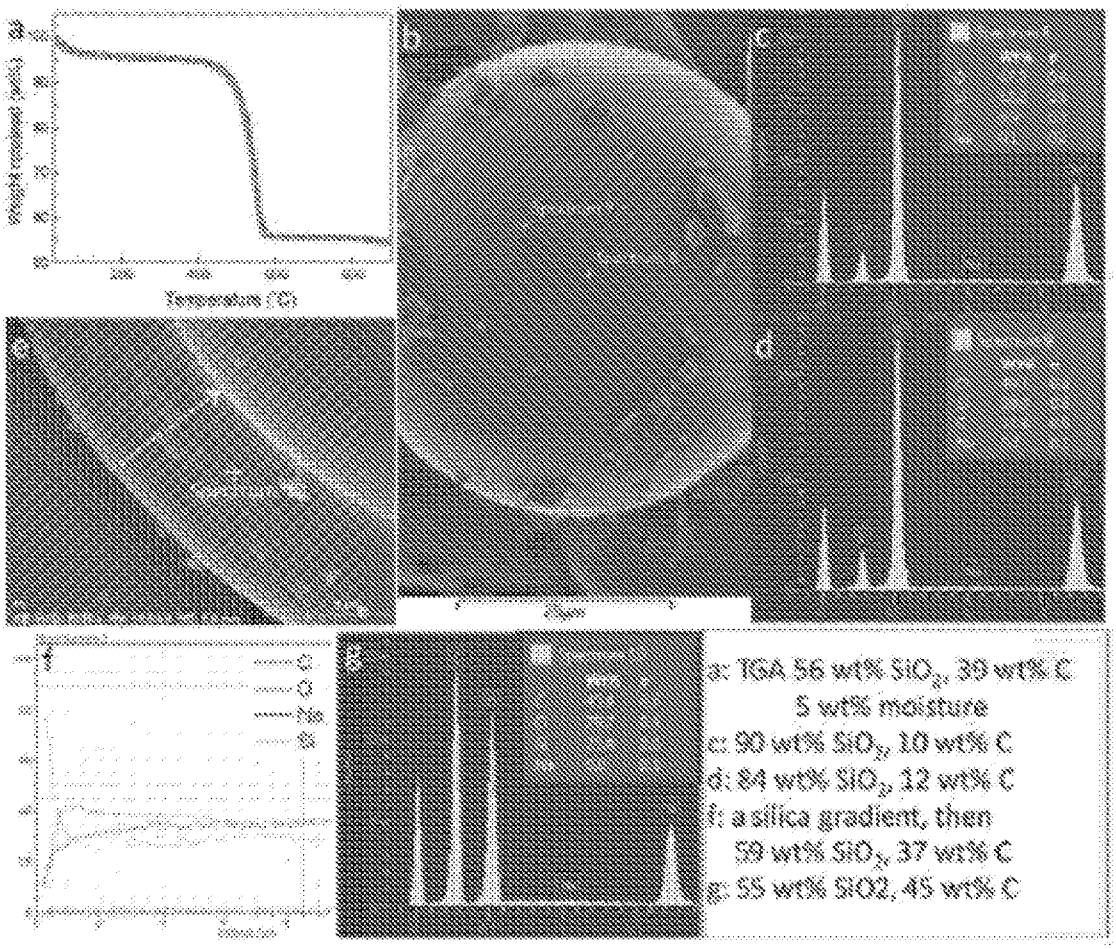

a: TGA 56 wt% SiO2, 39 wt% C
5 wt% moisture
c: 90 wt% SiO2, 10 wt% C
d: 84 wt% SiO2, 12 wt% C
f: a silica gradient, then
59 wt% SiO2, 37 wt% C
g: 55 wt% SiO2, 45 wt% C

Figure 11

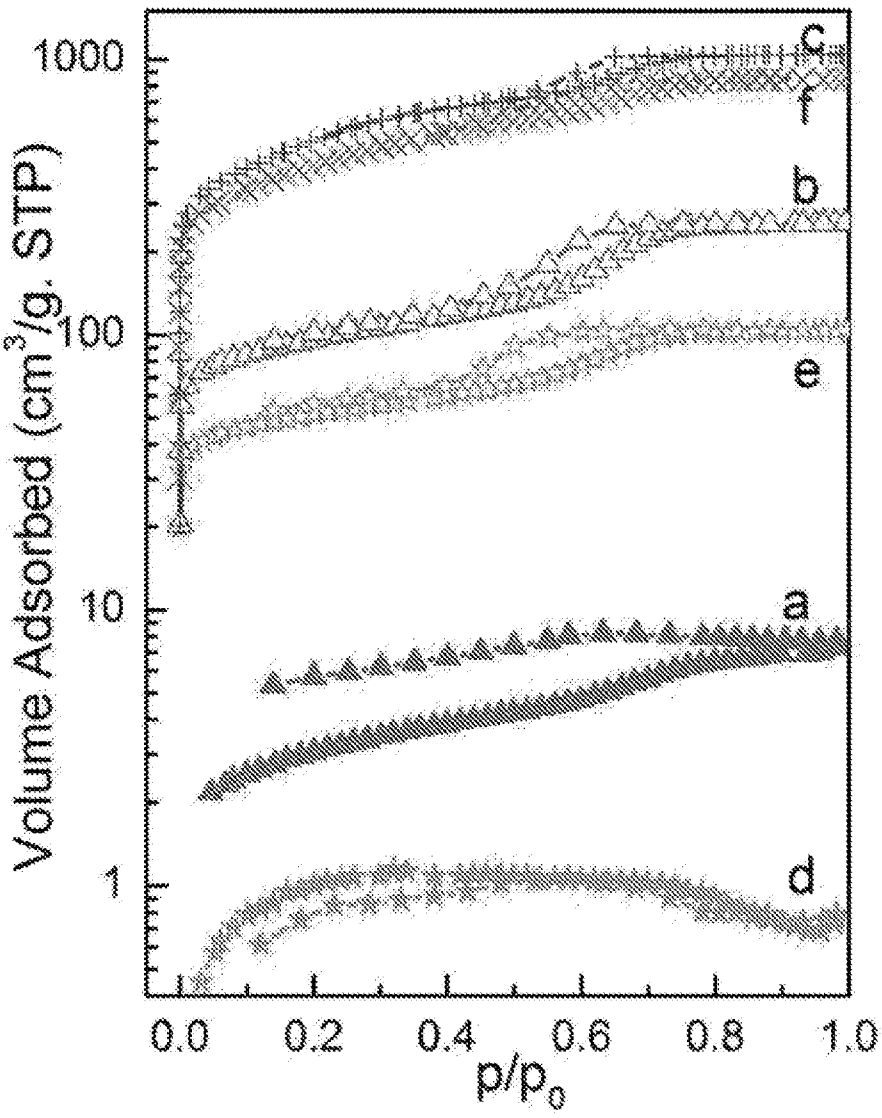

1000
100
10
1
Volume Adsorbed (cm3/g. STP)
0.0
0.2
0.4
0.6
0.8
1.0
p/p0
c
f
b
e
a
d

Figure 12

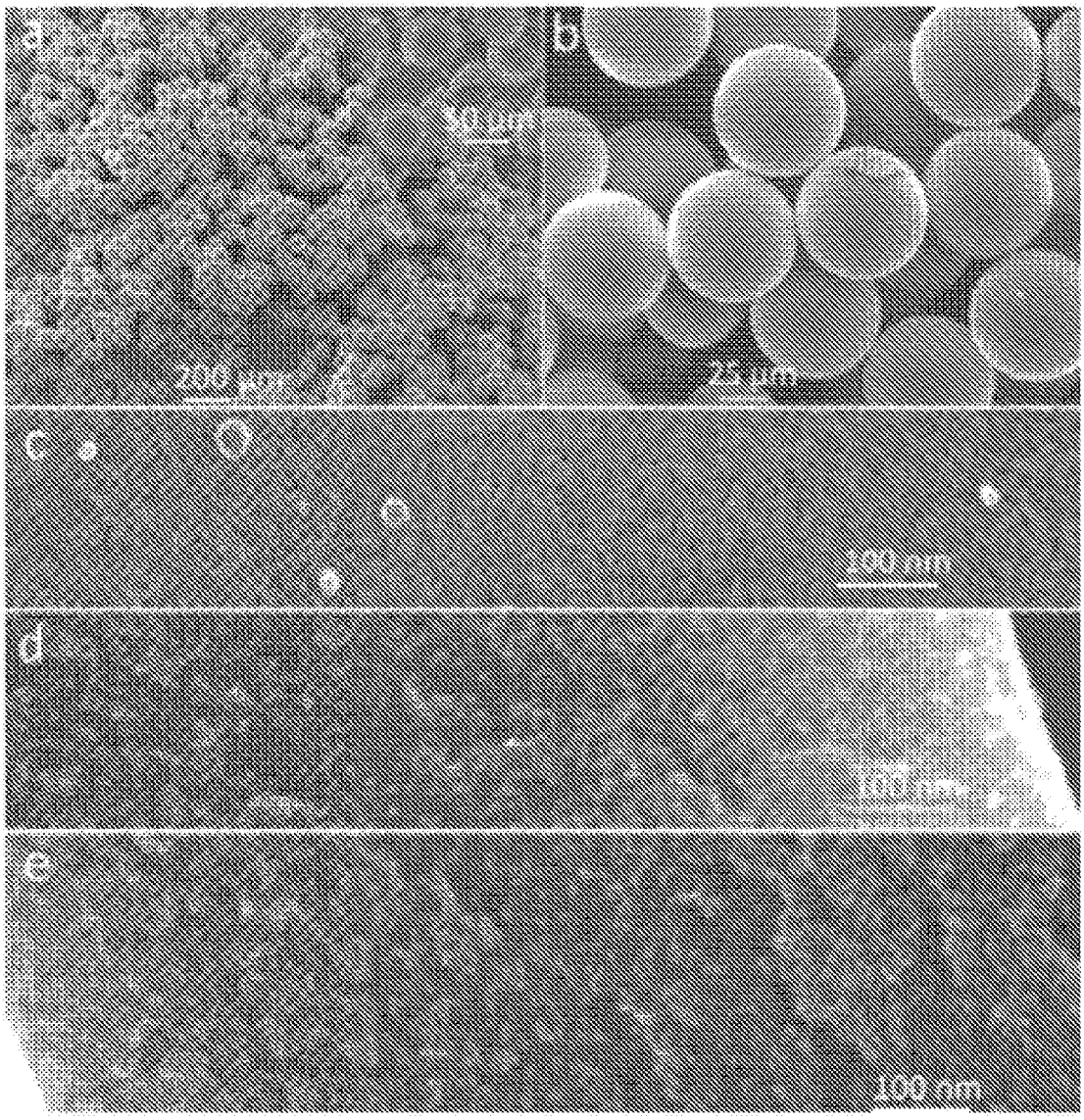


Figure 13

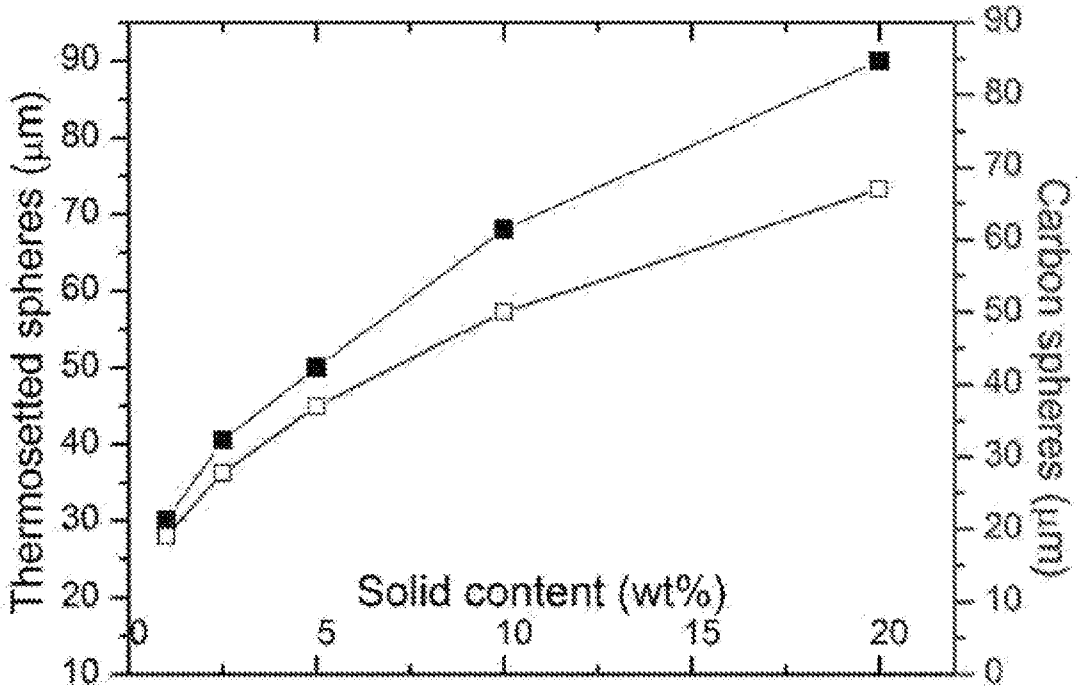

Thermosetted spheres (μm)
Carbon spheres (μm)
Solid content (wt%)
0
5
10
15
20
10
20
30
40
50
60
70
80
90
0
10
20
30
40
50
60
70
80
90

Figure 14

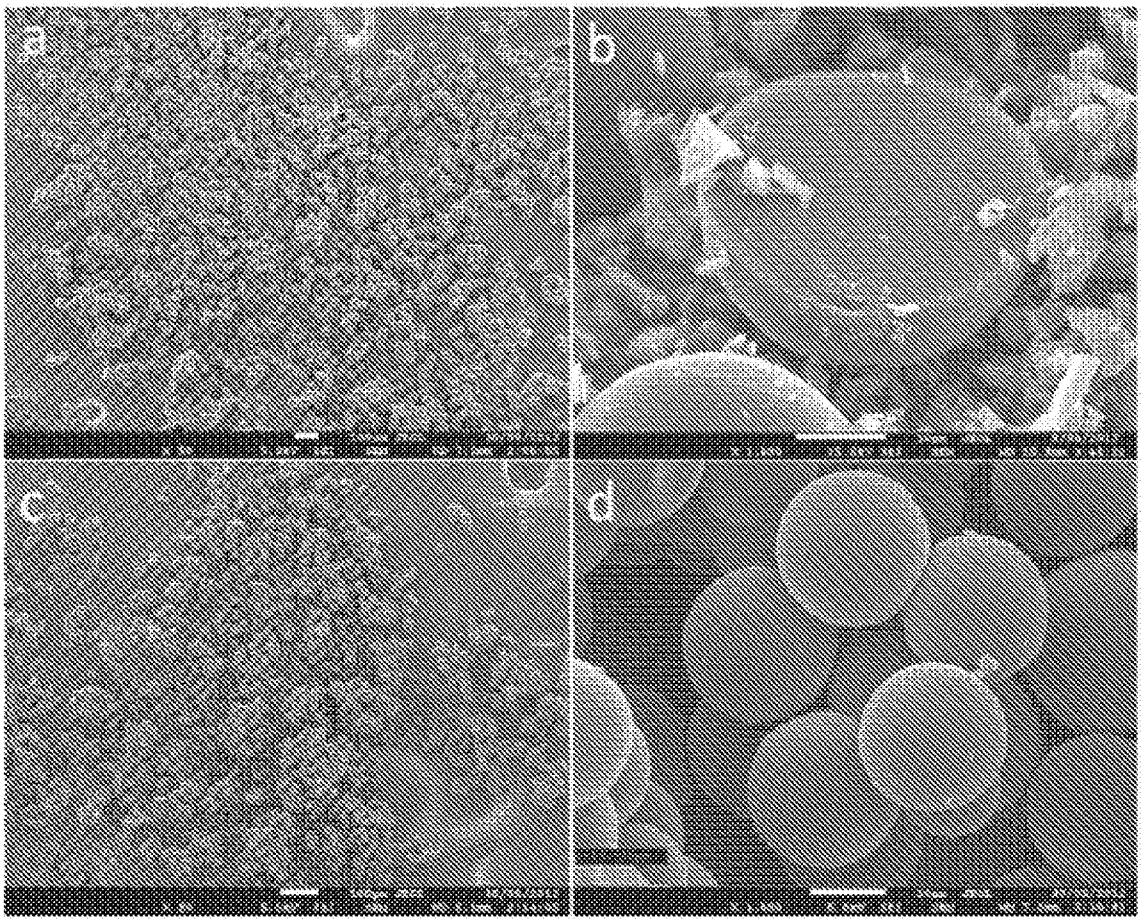


Figure 15

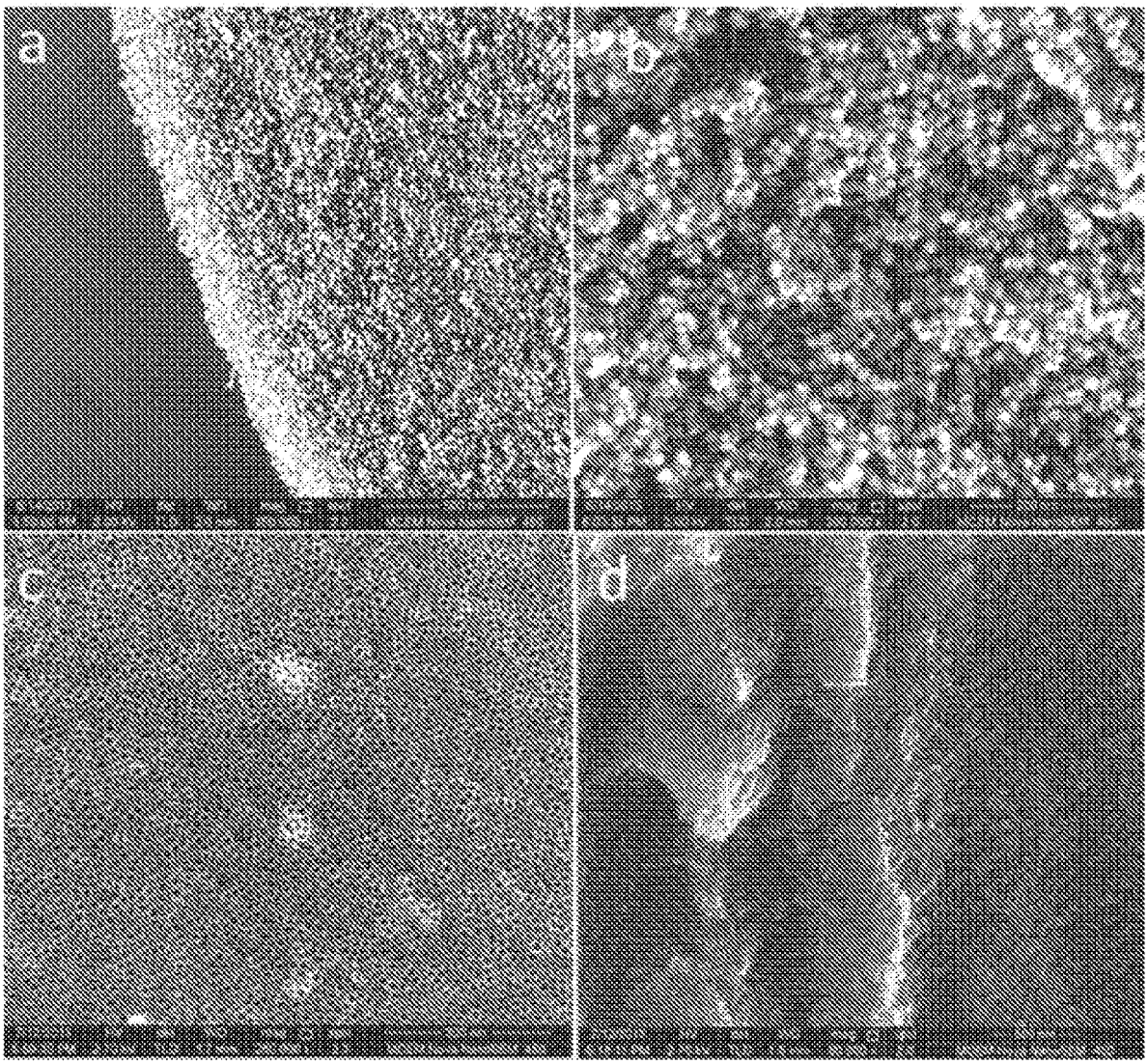


Figure 16

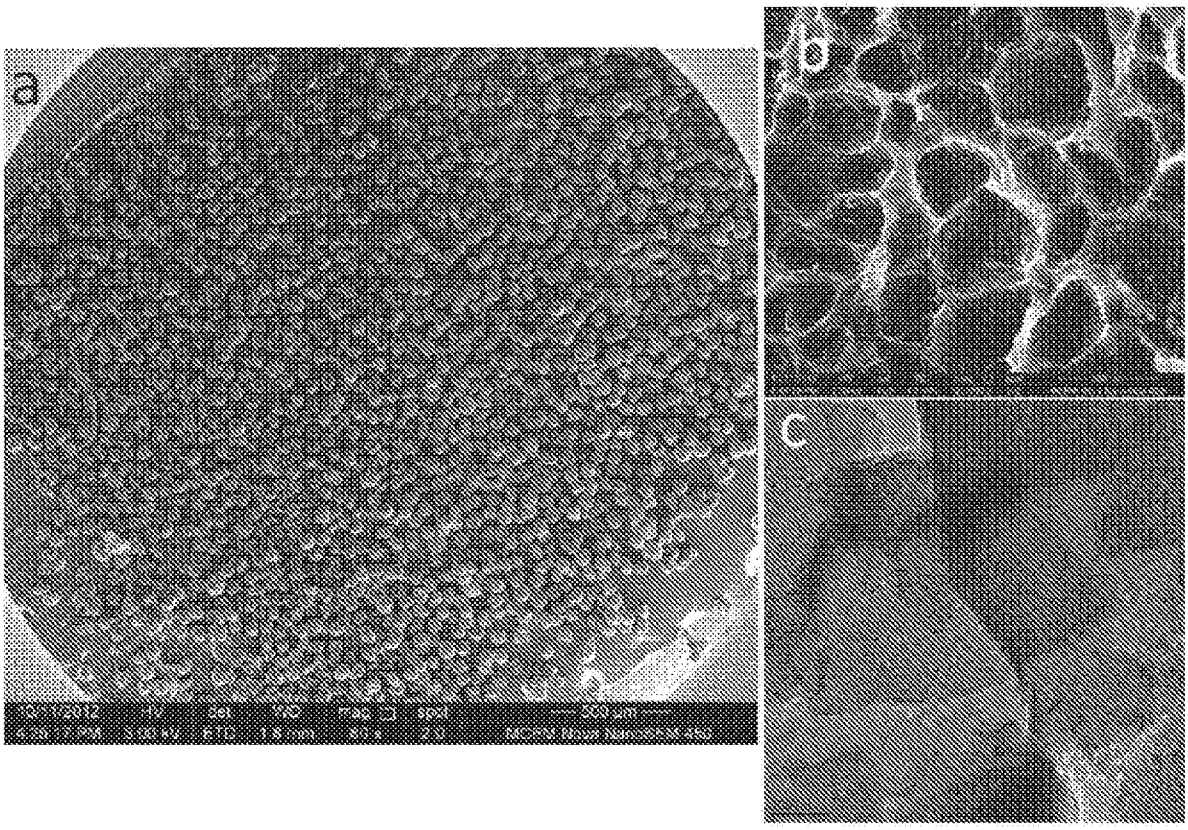


Figure 17

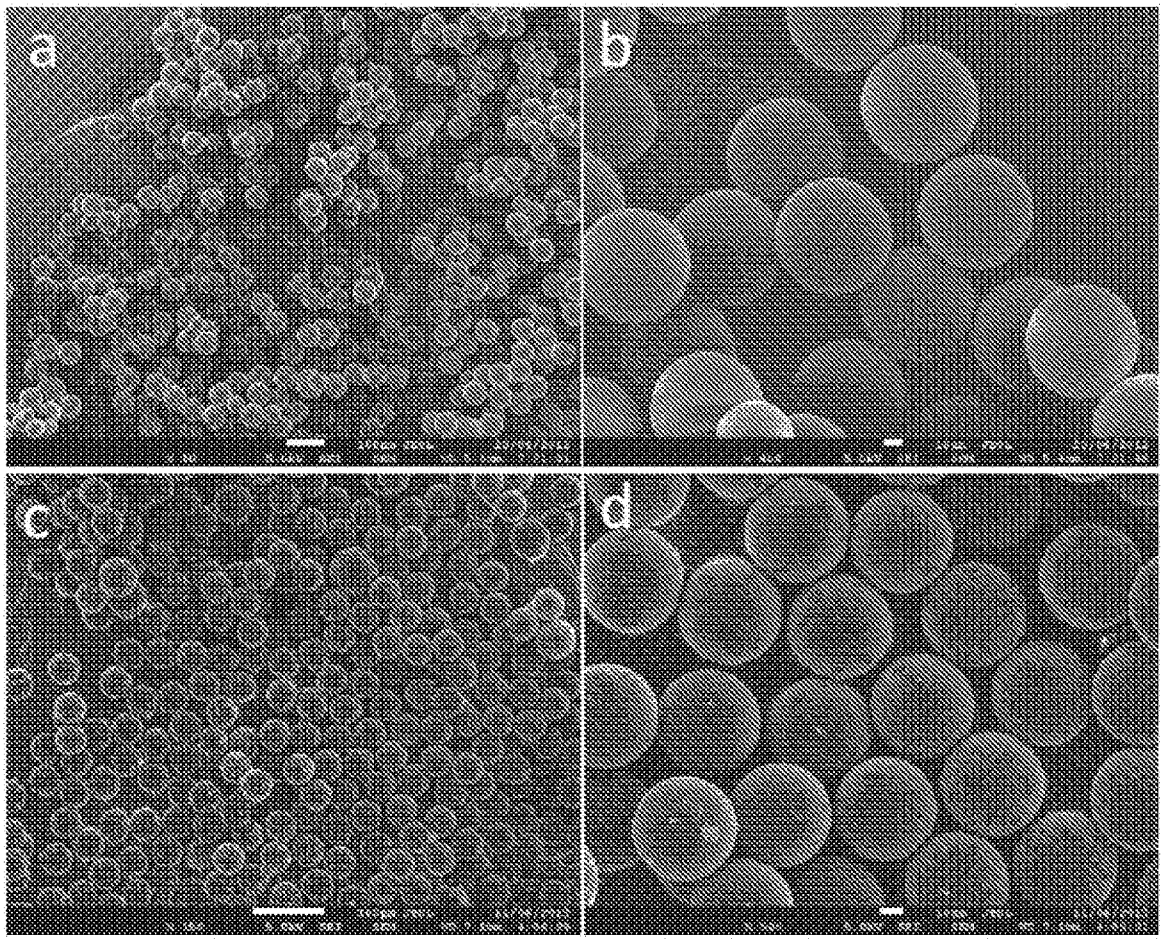


Figure 18

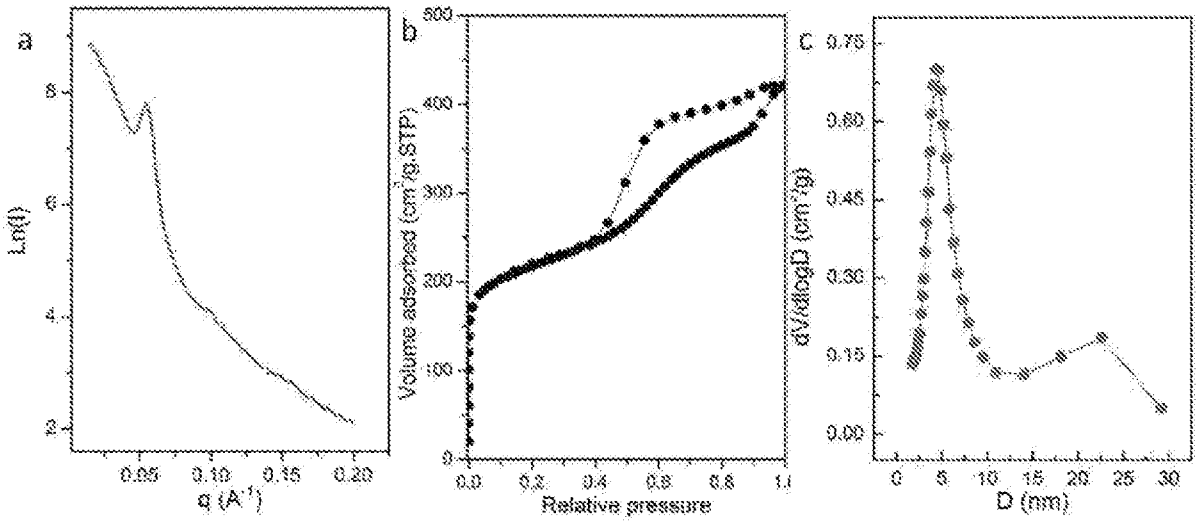

a
Ln(I)
q (A^{-1})
b
Volume adsorbed (cm^3/g STP)
Relative pressure
c
dV/dlogD (cm^3/g)
D (nm)

Figure 19

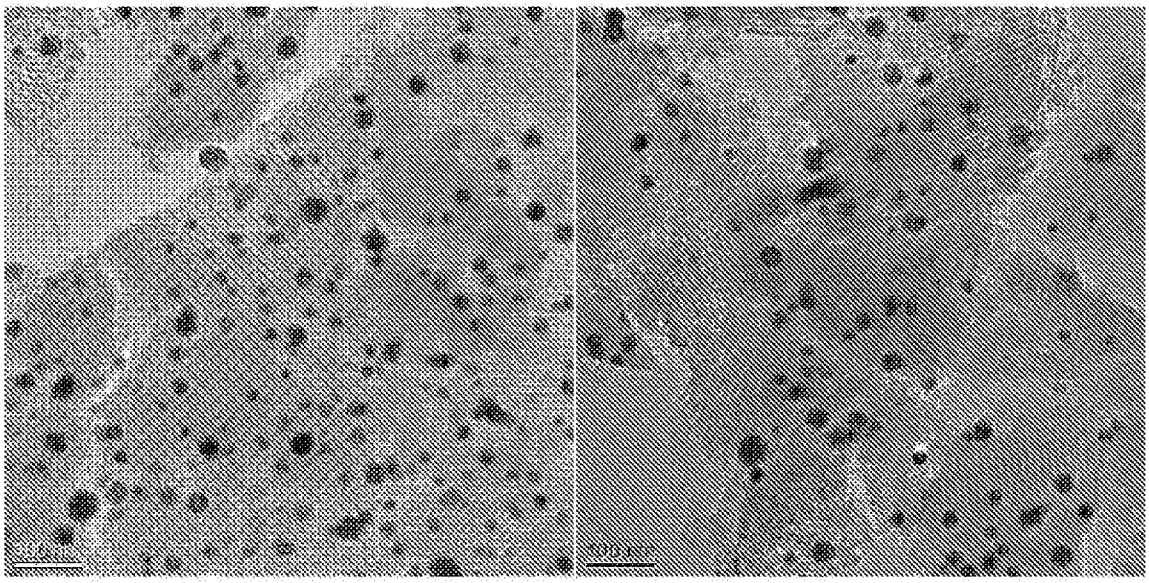


Figure 20

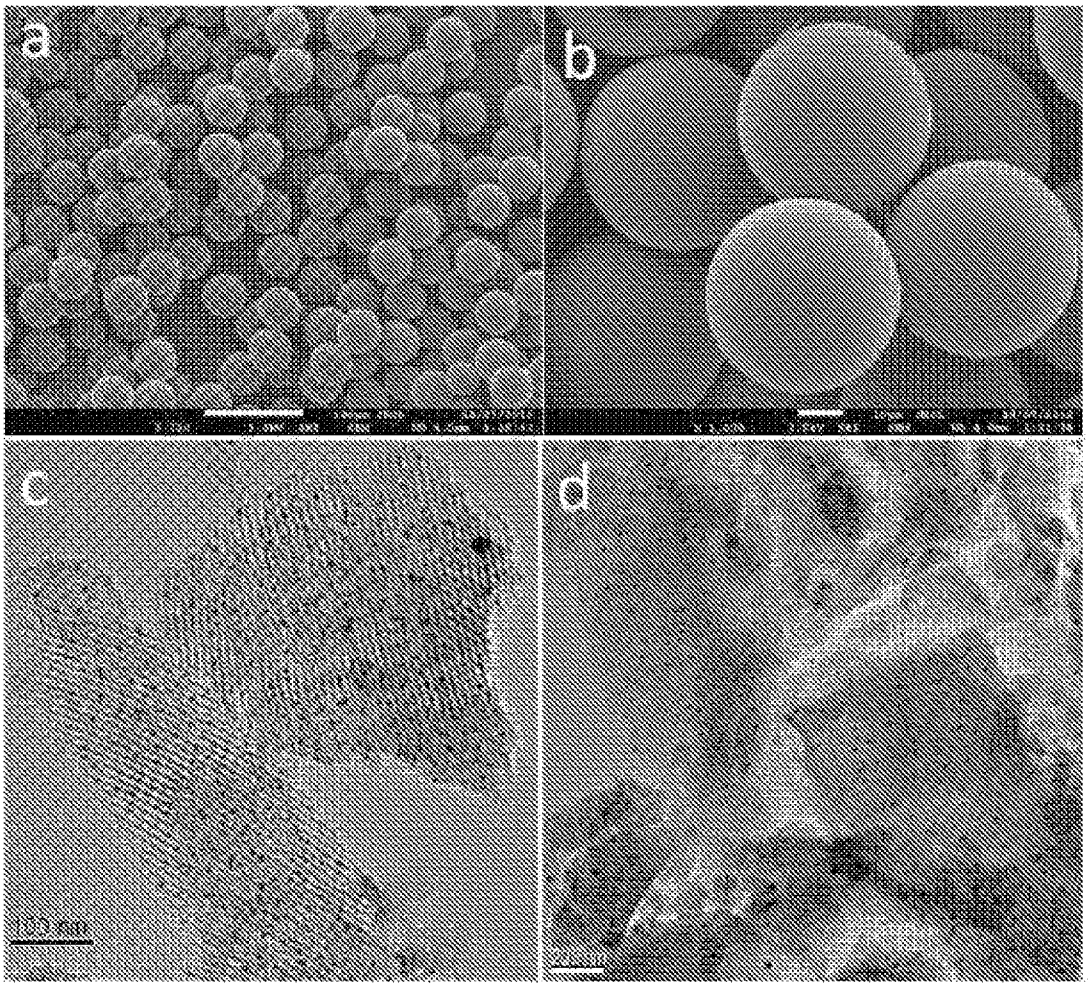


Figure 21

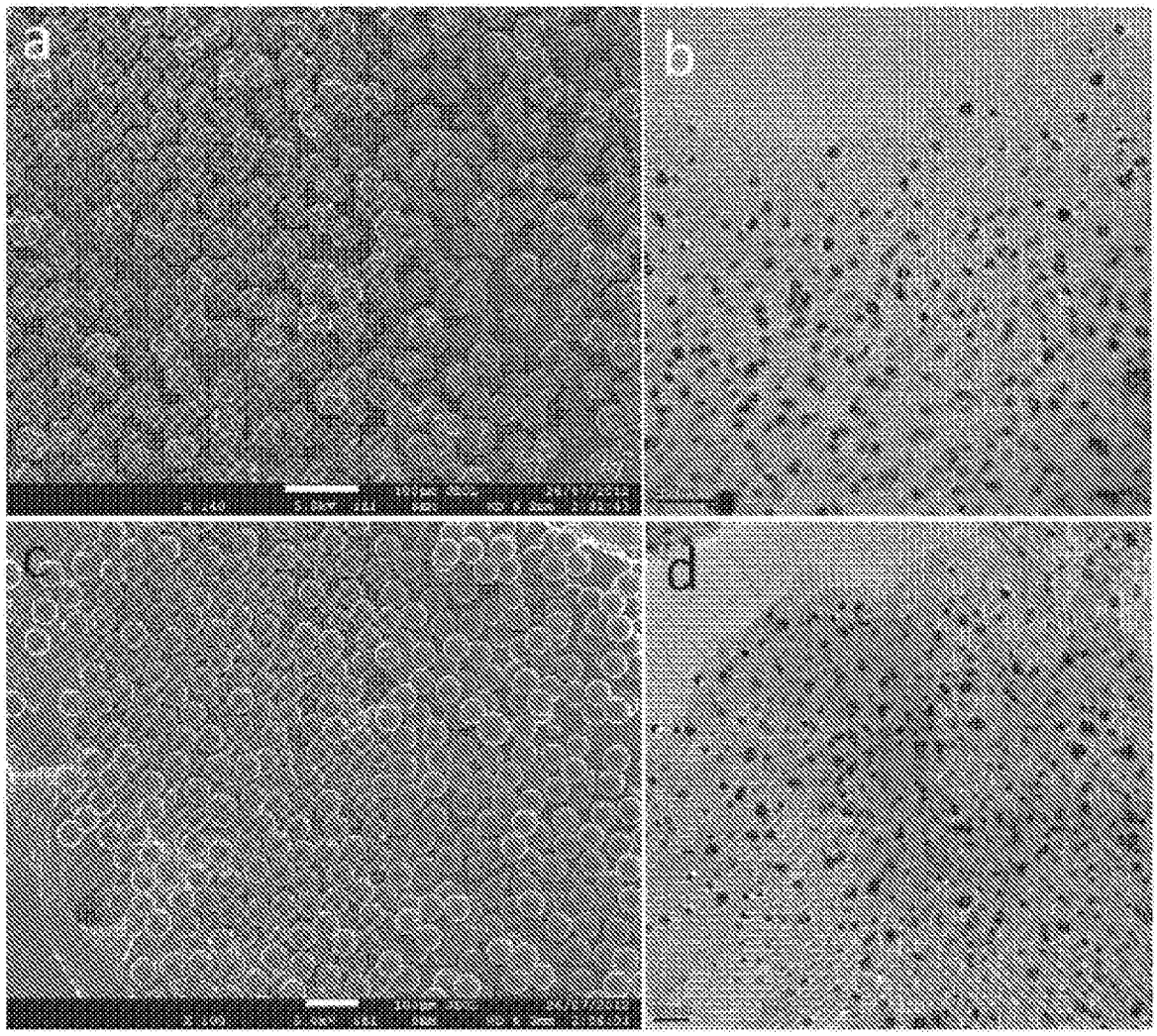


Figure 22

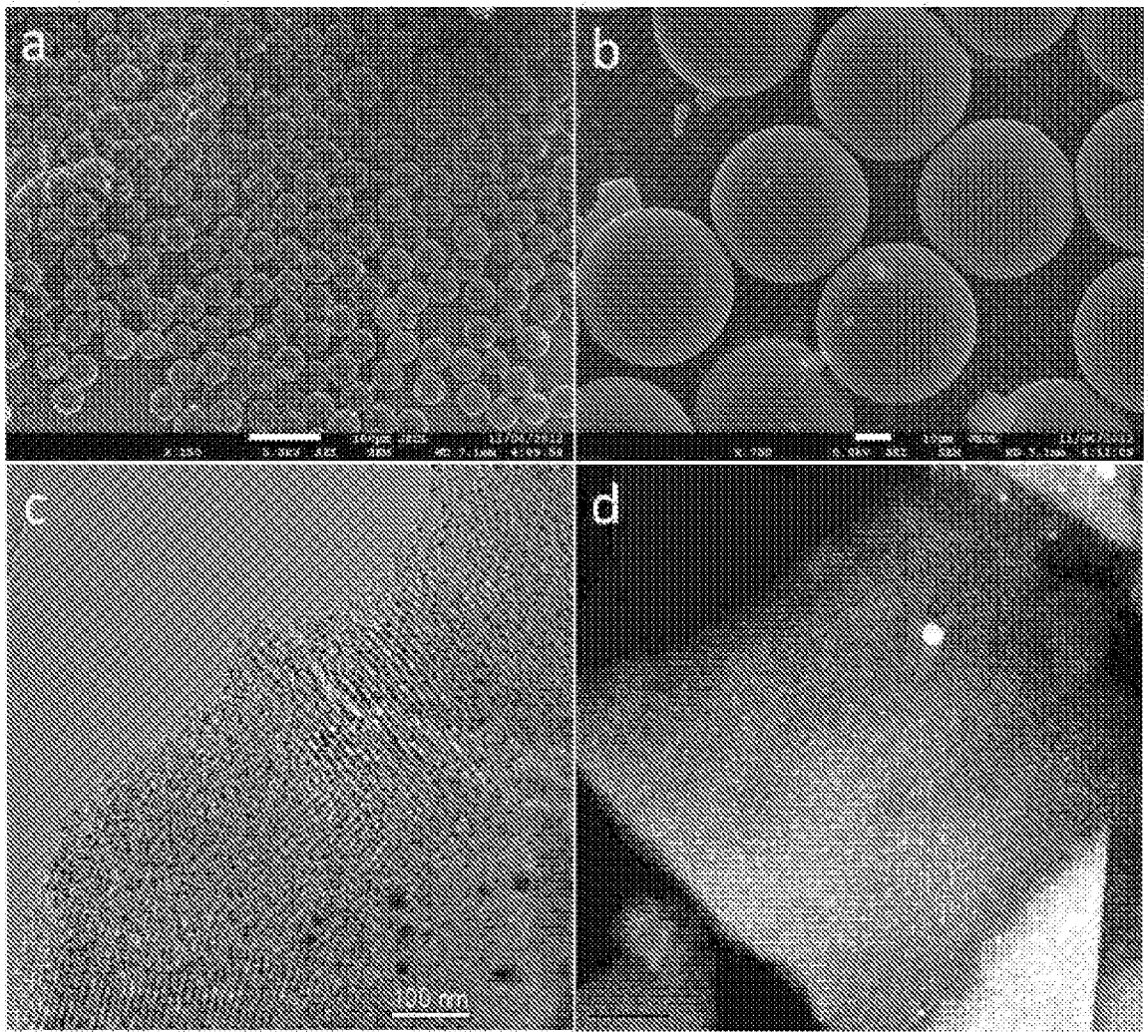


Figure 23

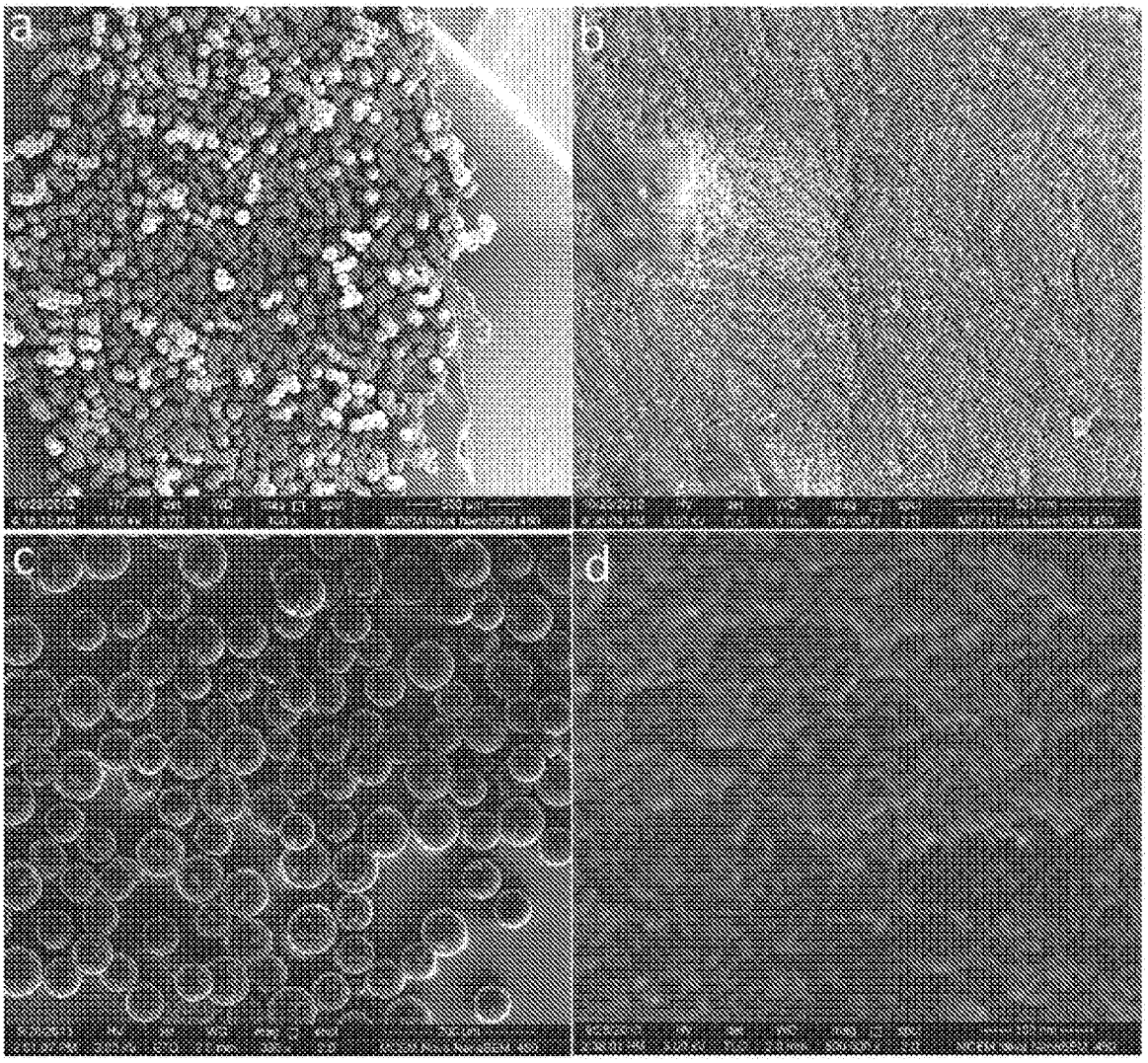
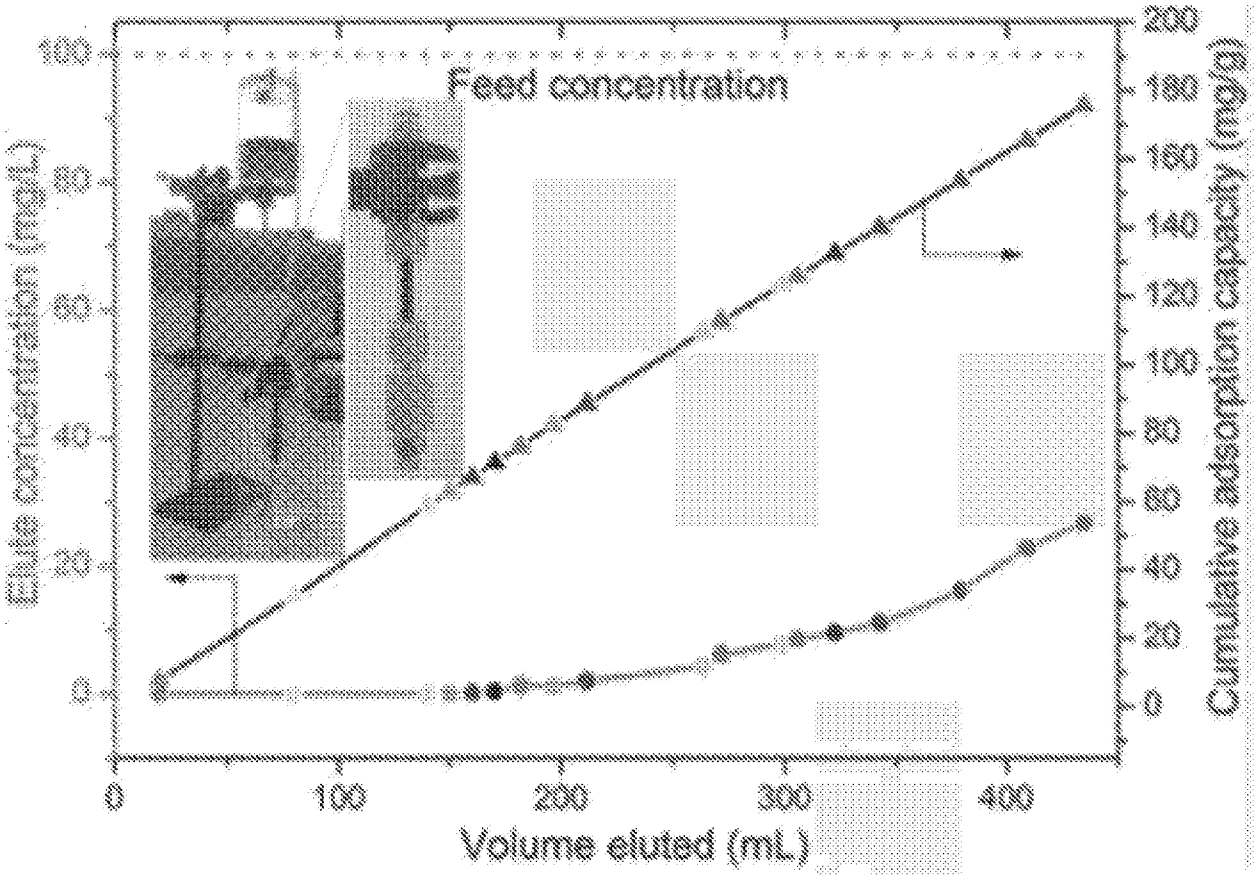


Figure 24


Feed concentration
Elute concentration (mg/L)
Cumulative adsorption capacity (mg/g)
Volume eluted (mL)
0
20
40
60
80
100
0
20
40
60
80
100
120
140
160
180
200
0
100
200
300
400

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2014/050293

A. CLASSIFICATION OF SUBJECT MATTER

B05D 5/00 (2006.01) B82B 1/00 (2006.01) B82Y 30/00 (2011.01) B82Y 40/00 (2011.01)

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)

WPI, EPODOC, TXTE, INSPEC: IPC/CPC Marks: B05D 5/00, B82B 1/00, B82Y 30/00, B82Y 40/00; keywords: microsphere, mesoporous, resin, sugar, polymer, carbohydrate, amine, amino, phenolic, melamine, polyurea, polyaniline, template, oxide, alkali metal, sodium chloride, NaCl, transition metal, silica, SiO2, silicon dioxide, alumina, Al2O3, locking agent, surface lock, alkoxide, nitrate, chloride, eject, spray, microfluidic, piezoelectric, pulse, nozzle, jet, droplet, frequency, Reynolds number, NRe, normalised ratio, solvent, water, ethanol, C2H5OH, evaporate, dry, monodisperse, unimodal, nano, nm and similar search terms; USPTO, Google Scholar, ScienceDirect & Google Patents using similar search terms. "Applicant/Inventor name search": "Monash University/ WU, Zhangxiong; WU, Duo; SELOMULYA, Cordelia; CHEN, Xiao Dong; ZHAO, Dongyuan" through AusPat and Esp@cenet.

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	

[X] Further documents are listed in the continuation of Box C [X] 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
23 December 2014	23 December 2014
Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Debashis Roy AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262256125

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2014/050293

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.

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/AU2014/050293**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/123517 A1 (THE ADMINISTRATORS OF THE TULANE EDUCATIONAL FUND) 22 August 2013 Abstract; page 3, lines 7-16; page 6, lines 13-19; Fig. 4; claims 65-66	1-36
X	US 2009/0155563 A1 (PETSEV et al.) 18 June 2009 Abstract; claim 1	36
X	CN 103342453 A (LIJUN et al.) 09 October 2013, English Abstract retrieved from EPODOC database Abstract	36

INTERNATIONAL SEARCH REPORT	International application No. PCT/AU2014/050293

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 1-35 are directed to a method for forming microspheres including: obtaining a precursor solution including a template, a carbon precursor, and a surface locking agent dissolved in a solvent; ejecting the precursor solution through a micro-fluidic spray nozzle to form droplets, wherein the droplets are ejected into a drying environment; evaporating at least some of the solvent from the droplets to form microspheres, the microspheres including the template, the carbon precursor or its derivative cross-linked product, and the surface locking agent or its derivative cross-linked product. It is considered that a method of making microspheres from a precursor solution including a template, a carbon precursor and a surface locking agent comprises a first distinguishing feature. The feature of a method of making microspheres from a precursor solution including a template, a carbon precursor and a surface locking agent is specific to this group of claims.

- Claim 36 is directed to a population of monodisperse mesoporous microspheres. It is considered that the product of microspheres comprises a second distinguishing feature. The feature of a population of monodisperse mesoporous microspheres is specific to this claim.

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. The only feature common to all of the claimed inventions is the product microsphere. However it is considered that this feature is generic in this particular art. See D2: US 2009/0155563 A1 (PETSEV et al.) 18 June 2009 (Abstract; claim 1); D3: CN 103342453 A (LIJUN et al.) 9 October 2013 (Abstract).

Therefore this common feature cannot be a special technical feature. Hence there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a posteriori*.

As the additional invention did not require significant additional search, this report is directed to all inventions.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2014/050293**

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**
WO 2013/123517 A1	22 August 2013		
US 2009/0155563 A1	18 June 2009	US 8334013 B2	18 Dec 2012
		US 8334014 B1	18 Dec 2012
CN 103342453 A	09 October 2013		

End of Annex

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