

SiO₂-LAYERED DOUBLE HYDROXIDE MICROSPHERES **AND METHODS OF MAKING THEM**

The present invention relates to new SiO₂-layered double hydroxide (LDH) microspheres and to methods of making the same.

Layered double hydroxides (LDHs) are a class of compounds which comprise two or more metal cations and have a layered structure. A review of LDHs is provided in *Structure and Bonding*; Vol. 119, 2005 *Layered Double Hydroxides* ed. X Duan and D.G. Evans. The hydrotalcites, perhaps the most well-known examples of LDHs, have been studied for many years. LDHs can intercalate anions between the layers of the structure.

Core shell particles are described in the literature by “core@shell” (for example by Teng *et al.*, Nano Letters, 2003, 3, 261-264, or by “core/shell” (for example J. Am. Chem Soc., 2001, 123, pages 7961-7962). We have adopted the “core@shell” nomenclature as it is emerging as the more commonly accepted abbreviation.

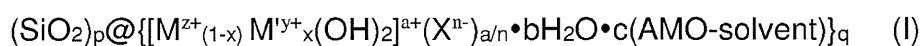
SiO₂/LDH core-shell microspheres are described by Shao *et al*, Chem. Mater. 2012, 24, pages 1192-1197. Prior to treatment with a metal precursor solution, the SiO₂ microspheres are primed by dispersing them in an Al(OOH) primer sol for two hours with vigorous agitation followed by centrifuging, washing with ethanol and drying in air for 30 minutes. This priming treatment of the SiO₂ microspheres was repeated 10 times before the SiO₂ spheres thus coated with a thin Al(OOH) film were autoclaved at 100°C for 48 hours in a solution of Ni(NO₃)₂•6H₂O and urea. Hollow SiO₂-NiAl-LDH microspheres obtained by this process were reported as exhibiting excellent pseudocapacitance performance. Unfortunately, the requirement for the Al(OOH) priming of the SiO₂ surface, prior to LDH growth, makes this process unsuitable for use on an industrial scale.

Chen *et al*, J. Mater. Chem. A, 1, 3877-3880 describes the synthesis of SiO₂@MgAl-LDHs having use in the removal of pharmaceutical pollutants from water. The synthesis described comprises coprecipitating LDH from a metal precursor solution containing the SiO₂ microspheres followed by

ultrasound assisted direct growth of LDH nanosheets on the surface of the SiO₂ microspheres. Unfortunately, the reported method does not allow the morphology of the surface LDHs to be tuned and the surface area of the product SiO₂@LDHs is not high.

It is an object of the present invention to provide a facile method of making SiO₂@LDH microspheres which overcomes drawbacks of the prior art, which in particular does not require a step of initially forming an Al(OOH) film on the SiO₂ surface prior to treatment with the metal precursor solution or the requirement for ultrasound assistance in achieving LDH growth on the SiO₂ surface. It is also an object of the present invention to provide SiO₂@LDHs wherein the thickness, size and morphology of the LDH layer can each be tuned easily for different applications. It is yet a further object of the present invention to provide SiO₂@LDHs that have high surface area.

This object is achieved by a method of making silica-layered double hydroxide microspheres having the general formula I



wherein,

M^{z+} and M^{y+} are two different charged metal cations;

z = 1 or 2;

y = 3 or 4;

0 < x < 0.9;

b is 0 to 10;

c is 0 to 10;

p > 0,

q > 0;

Xⁿ⁻ is an anion; with n > 0 (preferably 1-5)

a = z(1-x) + xy-2; and

the AMO-solvent is an 100% aqueous miscible organic solvent;

which method comprises the steps:

- (a) contacting silica microspheres and a metal ion containing solution containing metal ions M^{z+} and M^{y+} in the presence of a base and anion solution;

- (b) collecting the product; and
- (c) optionally treating the product with AMO-solvent and recovering the solvent treated material.

According to a further aspect of the invention, there is provided a silica-layered double hydroxide microsphere or a plurality thereof obtained, directly obtained or obtainable by a process defined herein.

A silica-layered double hydroxide microsphere is known to comprise a silica microsphere having solid LDH attached to its surface. Such a material, denoted as $\text{SiO}_2\text{@LDH}$, may be a core-shell material where the SiO_2 microsphere is a solid sphere, a yolk-shell material where the SiO_2 microsphere comprises an outer shell and a smaller SiO_2 sphere contained within the outer shell wherein there is a hollow portion between the smaller sphere and the inner surface of the outer shell, or a hollow shell material wherein the SiO_2 microsphere has a hollow interior.

In an embodiment, the process does not include a step of growing the LDH on the SiO_2 surface using ultrasound.

The SiO_2 microspheres used in the preparation of the $\text{SiO}_2\text{@LDH}$ microspheres according to the invention may be solid, yolk-shell or hollow microspheres and are commercially-available in a variety of sizes (diameters). However, SiO_2 microspheres may be prepared by a modified Stöber process involving ammonia catalysed hydrolysis and condensation of tetraethylorthosilicate using ethanol as solvent and cetyltrimethylammonium bromide as surfactant porogen, as is well known in the art.

In an embodiment, the silica microspheres do not contain any iron.

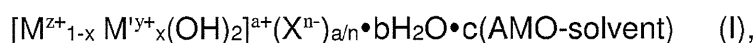
In another embodiment, the silica microspheres comprise greater than 75% w/w SiO_2 . Suitably, silica microspheres comprise greater than 85% w/w SiO_2 . More suitably, the silica microspheres comprise greater than 95% w/w SiO_2 . Most suitably, the silica microspheres comprise greater than 98% w/w SiO_2 .

In another embodiment, the silica microspheres consist essentially of SiO_2 .

In another embodiment, the silica microspheres consist of SiO_2 .

In another embodiment, the SiO₂ microspheres have an average diameter of between 0.15 µm and 8 µm. Suitably, the SiO₂ microspheres have an average diameter of between 0.15 µm and 2 µm. More suitably, the SiO₂ microspheres have an average diameter of between 0.15 µm and 1 µm. Most suitably, the SiO₂ microspheres have an average diameter of between 0.2 µm and 0.8 µm.

The LDH nanosheets grown on the surface of the SiO₂ microspheres comprise, and preferably consist of, LDH represented by the general formula I



wherein M^{z+} and M'^{y+} are different charged metal cations; z = 1 or 2; y = 3 or 4; 0 < x < 0.9; b = 0 – 10; c = 0 – 10, Xⁿ⁻ is an anion, n is the charge on the anion, n > 0 (preferably 1-5); a = z(1-x)+xy-2; and AMO-solvent is an 100% aqueous miscible organic solvent.

As stated above, M^{z+} and M'^{y+} are different charged metal cations. Having regard to the fact that z = 1 or 2, M will be either a monovalent metal cation or a divalent metal cation. When z = 1, M is either a single monovalent metal cation or two or more different monovalent metal cations. When z = 2, M is either a single divalent metal cation or two or more different divalent metal cations. In an embodiment, z = 2, i.e. M is one or more divalent metal cations. M', in view of the fact that y = 3 or 4, will be a trivalent metal cation or a tetravalent metal cation. When z = 3, M' is either a single trivalent metal cation or two or more different trivalent metal cations. When z = 4, M' is either a single tetravalent metal cation or two or more different tetravalent metal cations. In an embodiment, y = 3, i.e. M' is one or more trivalent metal cations.

A preferred example of a monovalent metal, for M, is Li. Examples of divalent metals, for M, include Ca, Mg, Zn, Fe, Co, Cu and Ni and mixtures of two or more of these. Preferably, the divalent metal M, if present, is Ca, Ni or Mg. Examples of metals, for M', include Al, Ga, In, Y and Fe. Preferably, M' is a trivalent cation, for example Al. Preferably, the LDH will be a Li-Al, an Mg-Al or a Ca-Al LDH.

The anion Xⁿ⁻ in the LDH is any appropriate inorganic or organic anion. Examples of anions that may be used, as Xⁿ⁻, in the LDH include carbonate,

hydroxide, nitrate, borate, sulphate, phosphate and halide (F^- , Cl^- , Br^- , I^-) anions. Preferably, the anion X^{n-} , is selected from CO_3^{2-} , NO_3^- and Cl^- .

The AMO-solvent is any aqueous miscible organic solvent, i.e. a solvent which is 100% miscible with water. Examples of suitable water-miscible organic solvents for use in the present invention include one or more of acetone, acetonitrile, dimethylformamide, dimethylsulfoxide, dioxane, ethanol, methanol, n-propanol, isopropanol, or tetrahydrofuran. Suitably, the water-miscible organic solvents for use in the present invention is selected from lower (1-3C) alkanols and acetone. Preferably, the AMO-solvent is methanol, ethanol or acetone, especially acetone and ethanol.

According to one preferred embodiment, the layered double hydroxides are those having the general formula I above

in which M^{z+} is a divalent metal cation;

M'^{y+} is a trivalent metal cation; and

each of b and c is a number > zero, which gives compounds optionally hydrated with a stoichiometric amount or a non-stoichiometric amount of water and/or an aqueous-miscible organic solvent (AMO-solvent), such as acetone or ethanol.

Preferably, in the LDH of the above formula, M is Mg or Ca and M' is Al. The counter anion X^{n-} is typically selected from CO_3^{2-} , OH^- , F^- , Cl^- , Br^- , I^- , SO_4^{2-} , NO_3^- and PO_4^{3-} . In a most preferred embodiment, the LDH will be one wherein M is Mg, M' is Al and X^{n-} is CO_3^{2-} .

In carrying out the method of the invention, preferably the SiO_2 microspheres are dispersed in an aqueous solution containing the desired anion salt, for example Na_2CO_3 . A metal precursor solution, i.e. a solution combining the required monovalent or divalent metal cations and the required trivalent cations may then be added, preferably drop-wise, into the dispersion of the SiO_2 microspheres. Preferably, the addition of the metal precursor solution is carried out under stirring. The pH of the reaction solution is preferably controlled within the pH range 8 to 12, typically 8-11, more preferably 9 to 10.

In an embodiment, the method of the present invention does not include ammonia.

The structure of the SiO₂@LDH microspheres can be controlled by the tendency of SiO₂ to dissolve or partially dissolve at higher temperatures and higher pH values. For instance, carrying out the addition of the metal precursor solution to the dispersion of SiO₂ microspheres at room temperature and at pH 10 gives solid SiO₂@LDH particles although by raising the temperature of the reaction solutions, for instance to 40°C, it is possible to obtain yolk shell SiO₂@LDH particles. By carrying out the reaction at room temperature but using a higher solution pH, e.g. pH 11, it is possible to produce hollow shell SiO₂@LDH particles.

Typically, NaOH may be used to adjust the pH of the solution.

During the reaction, the LDH produced from the metal precursor solution reaction is formed on the SiO₂ surfaces of the microspheres as nanosheets.

It is preferred that the temperature of the metal ion containing solution in step (a) is within a range of from 20 to 150°C. More preferably, from 20 to 80°C.

In a preferred embodiment, the silica-layered double hydroxide microspheres have specific surface area of at least 100 m²/g, preferably at least 177 m²/g, and more preferably at least 200 m²/g, and even more preferably at least 250 m²/g.

Suitably, the silica-layered double hydroxide microspheres comprise solid silica microsphere cores and have specific surface area of at least 100 m²/g.

Suitably, the silica-layered double hydroxide microspheres comprise yolk-shell microsphere cores and have specific surface area of at least 100 m²/g.

Suitably, the silica-layered double hydroxide microspheres comprise hollow-shell microsphere cores and have specific surface area of at least 130 m²/g.

Most preferred, the silica-layered double hydroxide microspheres have at least one structure from hollow-shell, yolk-shell and solid core-shell structures.

In a preferred embodiment, the silica-layered double hydroxide microspheres have a thickness of layered double hydroxide layer larger than 65 nm, preferably larger than 110 nm, more preferably larger than 160 nm.

The obtained solid product is collected from the aqueous medium. Examples of methods of collecting the solid product include centrifugation and filtration. Typically, the collected solid may be re-dispersed in water and then collected again. Preferably, the collection and re-dispersion steps are repeated twice.

The finally-obtained solid material may then be subjected to drying, for instance, in an oven for several hours.

In the event that a product containing AMO-solvent is required, the material obtained after the collection/re-dispersion procedure described above may be washed with, and preferably also re-dispersed in, the desired solvent, for instance acetone or ethanol. If re-dispersion is employed, the dispersion is preferably stirred. Stirring for more than 2 hours in the solvent is preferable. The final product may then be collected from the solvent and then dried, typically in an oven for several hours.

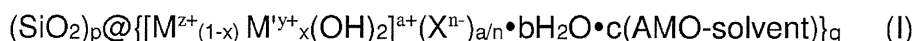
In an embodiment, the LDH layer is formed *in situ*. Suitably, the LDH is formed and coated onto the silica microspheres *in situ*.

The growth of LDH nanosheets on the surface of the SiO₂ microspheres is “tuneable”. That is to say, by varying the chemistry of the precursor solution, pH of the reaction medium and the rate of addition of the precursor solution to the dispersion of SiO₂ microspheres, the extent of, and the length and/or thickness of, the LDH nanosheets formed on the SiO₂ surface can be varied.

The production of the SiO₂@LDH microspheres according to the invention can be carried out as a batch process or, with appropriate replenishment of reactants, as a continuous process.

The products of the method of the present invention where the $\text{SiO}_2\text{@LDHs}$ are treated with solvent, i.e. the products having the formula I above where c is greater than zero, are a solution to the problem underlying the present invention *per se*.

Thus, according to a further aspect, the present invention provides silica-layered double hydroxide microspheres having the formula I



wherein,

M^{z+} and M'^{y+} are two different charged metal cations;

$z = 1$ or 2 ;

$y = 3$ or 4 ;

$0 < x < 0.9$;

b is 0 to 10;

c is 0 to 10;

$p > 0$,

$q > 0$;

X^{n-} is an anion; with $n > 0$ (preferably 1-5)

$a = z(1-x) + xy-2$; and

AMO-solvent is an 100% aqueous miscible organic solvent.

M' in formula I above is preferably Al.

M in formula I above is preferably Li, Mg, Ga, In, Ni, Co, Cu or Ca, more preferably Mg or Ni.

According to an embodiment, X^{n-} in formula I above is selected from carbonate, nitrate, borate, sulphate, phosphate, hydroxide and halide anions (F^- , Cl^- , Br^- , I^-). Preferably, the anion X^{n-} is selected from CO_3^{2-} , NO_3^- and Cl^- .

According to a particularly preferred embodiment, the $\text{SiO}_2\text{@LDH}$ microspheres of the invention contain LDH having the formula I above in which M is Mg, M' is Al and X^{n-} is CO_3^- .

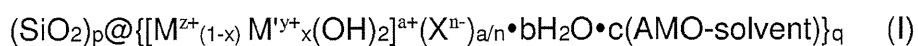
The AMO-solvent in formula I above is one that is miscible in water, especially one that is 100% miscible in water. Examples of solvents that can be used include methanol, ethanol and acetone. According to a preferred embodiment of the invention, the solvent is ethanol or acetone.

SiO₂@LDHs according to the present invention may be used as catalysts and/or catalyst supports.

Particularly preferred embodiments

The following represent particular embodiments of the silica-layered double hydroxide:

1.1 The silica-layered double hydroxide microspheres have the general formula I



wherein,

M^{z+} is selected from Li⁺, Ca²⁺, Ni²⁺ or Mg²⁺, and M'^{y+} is Al³⁺ or Fe³⁺;

0 < x < 0.9;

b is 0 to 10;

c is 0 to 10;

p > 0,

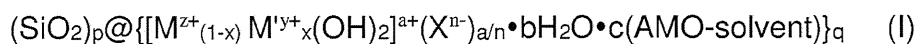
q > 0;

Xⁿ⁻ is selected from carbonate, hydroxide, nitrate, borate, sulphate, phosphate and halide (F⁻, Cl⁻, Br⁻, I⁻) anions; with n > 0 (preferably 1-5)

a = z(1-x) + xy-2; and

the AMO-solvent is selected from a lower (1-3C) alkanol (e.g. ethanol) or acetone.

1.2 The silica-layered double hydroxide microspheres have the general formula I



wherein,

M^{z+} is selected from Li⁺, Ca²⁺, Ni²⁺ or Mg²⁺, and M'^{y+} is Al³⁺;

0 < x < 0.9;

b is 0 to 10;

c is 0 to 10;

p > 0,

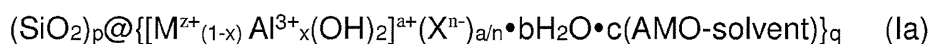
q > 0;

Xⁿ⁻ is selected from CO₃²⁻, NO₃⁻ or Cl⁻; with n > 0 (preferably 1-5)

$$a = z(1-x) + xy-2; \text{ and}$$

the AMO-solvent is acetone or ethanol.

- 1.3 The silica-layered double hydroxide microspheres have the general formula Ia



wherein,

M^{z+} is selected from Li^+ , Ca^{2+} , Ni^{2+} or Mg^{2+} ;

$$0 < x < 0.9;$$

b is 0 to 10;

c is 0 to 10;

$$p > 0,$$

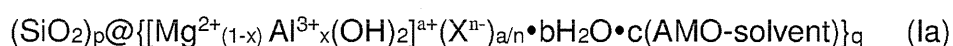
$$q > 0;$$

X^{n-} is selected from CO_3^{2-} , NO_3^- or Cl^- ; with $n > 0$ (preferably 1-5)

$$a = z(1-x) + xy-2; \text{ and}$$

the AMO-solvent is acetone or ethanol.

- 1.4 The silica-layered double hydroxide microspheres have the general formula Ia



wherein,

$$0 < x < 0.9;$$

b is 0 to 10;

c is 0 to 10;

$$p > 0,$$

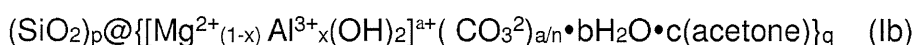
$$q > 0;$$

X^{n-} is selected from CO_3^{2-} , NO_3^- or Cl^- ; with $n > 0$ (preferably 1-5)

$$a = z(1-x) + xy-2; \text{ and}$$

the AMO-solvent is acetone or ethanol.

- 1.5 The silica-layered double hydroxide microspheres have the general formula Ib

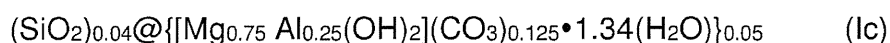


wherein,

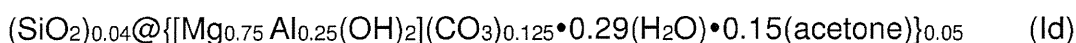
$$0 < x < 0.9;$$

b is 0 to 10;
 c is 0 to 10;
 $p > 0$,
 $q > 0$;
 $a = z(1-x) + xy-2$.

1.6 The silica-layered double hydroxide microspheres have the general formula 1c



1.7 The silica-layered double hydroxide microspheres have the general formula 1d



Preferred, suitable, and optional features of any one particular aspect of the present invention are also preferred, suitable, and optional features of any other aspect.

FIGURES

Figure 1. XRD patterns showing three sizes of silica nanoparticles (a) 300nm, (b) 550nm and (c) 800nm.

Figure 2. TGA curves of differently sized silica nanoparticles (a) 800nm, (b) 550nm and (c) 300nm.

Figure 3. SEM images of 800nm silica microspheres prepared via seeded growth.

Figure 4. XRD patterns of (a) 550nm silica microspheres, (b) LDH nanoparticles and (c) SiO_2 @LDH microspheres ((b) and (c) were synthesized according to example 1).

- Figure 5. Percentage weight loss of (a) LDH, (b) SiO₂@LDH microspheres and (c) silica nanoparticles ((a) and (b) were synthesized according to example 1).
- Figure 6. ²⁹Si Solid-state NMR of (a) silica microspheres and (b) SiO₂@LDH microspheres ((b) were synthesized according to example 1).
- Figure 7. XRD patterns of SiO₂@LDH microspheres prepared at different pH conditions (a) ammonia method (example 4), (b) pH 9, (c) pH 10 and (d) pH 11 ((b)-(d): example 1).
- Figure 8. TGA of SiO₂@LDH microspheres prepared at different pH conditions (a) pH 11, (b) pH 10, (c) ammonia method and (d) pH 9.
- Figure 9. TEM images of SiO₂@LDH microspheres synthesized according to example 1 except at different temperatures (a) room temperature (b) 40°C.
- Figure 10. TGA and dTGA curves of SiO₂@LDH microspheres prepared according to example 1 except at different temperature (a) room temperature and (b) 40°C, (i) TGA curve, (ii) dTGA curve.
- Figure 11. Solid state NMR (a) ²⁹Si (b) ²⁷Al. SiO₂ @ LDH prepared according to example 1 except at different temperature (i) at room temperature (ii) at 40°C.
- Figure 12. XRD patterns of SiO₂@LDH microspheres prepared with different Mg:Al ratios (a) 1:1 (example 2), (b) 3:1 (example 3).
- Figure 13. XRD patterns of SiO₂@LDH microspheres prepared according to example 1 (a) conventional water washing (b) acetone washing.

Figure 14. TGA of SiO₂@LDH microspheres prepared according to example 2 (a) conventional water washing (b) acetone washing.

Figure 15. TEM image of SiO₂@LDH microspheres with different ratio of Mg/Al (a) 1:1 (example 2), (b) 2:1 (example 1) and (c) 3:1 (example 3).

Figure 16. TEM image of SiO₂@LDH microspheres according to example 1 except with different size of silica (a) 300nm, (b) 550nm and (c) 800nm.

Figure 17. TEM image of SiO₂@LDH microspheres with different morphology (a) solid (example 1), (b) yolk-shell (example 1 at 40 °C) and (c) hollow (example 1 at pH 11).

Figure 18. XRD patterns of SiO₂@AMO-LDH with an Mg : Al = 3:1 (a) pH=10 and room temperature (b) pH=10 and 40 °C (c) pH=11 and 40 °C.

Figure 19. XRD patterns of SiO₂@AMO-LDH with Mg : Ni : Al = 2.7 : 0.3 : 1 (a) pH=10 and room temperature (b) pH=10 and 40 °C (c) pH=11 and 40 °C.

Figure 20. XRD patterns of SiO₂@AMO-LDH with an Mg : Al : Fe = 3 : 0.9 : 0.1 (a) pH=10 and room temperature (b) pH=10 and 40 °C (c) pH=11 and 40 °C;

Figure 21. TEM image of SiO₂@AMO LDH microspheres according to examples 5 and 7 at pH=10 and room temperature (a) Mg : Al=3:1 (b) Mg : Al : Fe = 3 : 0.9 : 0.1.

Figure 22. TEM image of SiO₂@AMO-LDH with Mg : Ni : Al=2.7 : 0.3 : 1 microspheres with different morphology according to example 6

(a) pH=10 and room temperature (b) pH=10 and 40 °C (c) pH=11 and 40 °C

EXPERIMENTAL METHODS

1. General Details

1.1 Powder X-ray Diffraction

Powder X-ray diffraction (XRD) data were collected on a PANAnalytical X'Pert Pro diffractometer in reflection mode and a PANAnalytical Empyrean Series 2 at 40 kV and 40 mA using Cu K α radiation ($\alpha_1 = 1.54057 \text{ \AA}$, $\alpha_2 = 1.54433 \text{ \AA}$, weighted average = $1.54178 \text{ \AA}$). Scans were recorded from $5^\circ \leq 2\theta \leq 70^\circ$ with varying scan speeds and slit sizes. Samples were mounted on stainless steel sample holders. The peaks at $43\text{--}44^\circ$ are produced by the XRD sample holder and can be disregarded.

1.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) measurements were collected using a Netzsch STA 409 PC instrument. The sample (10 – 20 mg) was heated in a corundum crucible between 30°C and 800°C at a heating rate of 5°C min^{-1} under a flowing stream of nitrogen.

1.3 Solid State NMR Spectroscopy

^{29}Si and ^{27}Al MAS NMR spectra were recorded on a Varian Chemagnetics CMX Infinity 200 (4.7 T). Samples were packed in 7.5 mm zirconia rotors. A double resonance MAS probe was used for all measurements and a MAS rate of 4 kHz for ^{29}Si , whereas MAS rate of 6 kHz was used for ^{27}Al . ^{27}Al MAS NMR spectra were acquired with a single pulse excitation applied using a short pulse length (0.7 μs). Each spectrum resulted from 2000 scans separated by 1 s delay. The ^{27}Al chemical shifts are referenced to an aqueous solution of $\text{Al}(\text{NO}_3)_3$ ($\delta = 0 \text{ ppm}$). In order to obtain the quantitative ^{29}Si DPMAS NMR spectra, 5000 transients were typically acquired with an acquisition time of 68 ms (1024 data points zero filled to 16K) and recycle delay of 30 s. All ^{29}Si spectra were externally referenced to kaolinite (taken to

be at $\delta = -91.7$ ppm on a scale where $\delta(\text{TMS}) = 0$ ppm) as a secondary reference.

1.4 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) analysis was performed on a JEOL 2100 microscope with an accelerating voltage of 200 kV. Particles were dispersed in water or ethanol with sonication and then cast onto copper grids coated with carbon film and left to dry.

1.5 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) analysis was performed on a JEOL JSM 6610 scanning electron microscope. Particles were dispersed in water and cast onto a clean silica wafer. Before imaging, the samples were coated with a thin platinum layer to prevent charging and to improve the image quality. Energy dispersive X-ray spectroscopy (EDX), also carried out on this instrument, was used to determine the relative quantities of constituent elements on the surface of the sample.

1.6 Brunauer-Emmett-Teller Surface Area Analysis

Brunauer-Emmett-Teller (BET) specific surface areas were measured from the N_2 adsorption and desorption isotherms at 77 K collected from a Quantachrome Autosorb surface area and pore size analyser.

Example 1

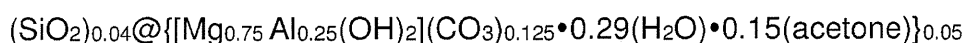
Silica spheres (100 mg, 550 nm) were dispersed in deionised water (20 mL) using ultrasound treatment. After 30 min., Na_2CO_3 (0.96 mmol) was added to the solution and a further 5 min of sonication was carried out to form solution A. Next an aqueous solution (19.2 mL) containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.96 mmol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.48 mmol) was added at a rate of 60 mL/h to solution A under vigorous stirring at room temperature. The pH of the reaction solution was controlled to be 10 with the addition of 1 M NaOH. The obtained solid was collected with centrifugation at 4000 rpm for 5 min and then re-

dispersed in deionised water (40 mL) and stirred for 1 h. The collection and re-dispersion were repeated twice. Afterward, the solid was washed with acetone (40 mL) and then re-dispersed in acetone (40 mL) and left to stir overnight. The solid was then dried under vacuum.

The SiO₂@LDH obtained in this Example, before the treatment with acetone, has the formula:-



The SiO₂@AMO-LDH, obtained after acetone treatment, has the formula:-



Yolk shell particles were obtained by carrying out the addition of the aqueous solution containing the Mg(NO₃)₂•6H₂O and Al(NO₃)₃•9H₂O at 40°C and pH10.

Hollow shell particles were obtained by carrying out the addition of the aqueous solution containing Mg(NO₃)₂•6H₂O and Al(NO₃)₃•9H₂O at room temperature but at pH11.

Surface Area Analysis

The solid SiO₂@LDH, the yolk shell SiO₂@LDH and the hollow shell SiO₂@LDH prepared as described above but without acetone treatment were subjected to Brunauer-Emmett-Teller (BET) surface area analysis.

The N₂ BET surface areas of the products were:

	<u>BET surface area (m²g⁻¹)</u>
Solid (i.e. core-shell) SiO ₂ @LDH	107
Yolk-shell SiO ₂ @LDH	118
Hollow-shell SiO ₂ @LDH	177

The BET surface areas reported above may be favourably compared to those of SiO₂@LDHs prepared according to (A) Shao *et al.* Chem. Mater. 2012, 24,

pages 1192-1197 and to those of SiO₂@LDHs prepared according to (B) Chen *et al.* J. Mater. Chem. A, 1, 3877-3880.

(A) SiO₂ microspheres pre-treated with Al(OOH).

Product SiO₂@NiAl LDH.

	<u>BET surface area (m²g⁻¹)</u>
Solid (i.e. core-shell) SiO ₂ microspheres	42.3
Yolk-shell SiO ₂ @LDH microspheres	68
Hollow-shell SiO ₂ @LDH microspheres	124

(B) SiO₂ microspheres – no pre-treatment – ammonia method.

Product SiO₂@LDH.

	<u>BET surface area (m²g⁻¹)</u>
Solid (i.e. core-shell) SiO ₂ @LDH microspheres	61

Core-shell SiO₂@LDHs were prepared according to the procedures described in Example 1 and in the Examples 2 and 3 below having different thicknesses of LDH layer. The ratio of Mg/Al was varied to control the thickness of the LDH layer. A Mg:Al ratio of 1:1 was found to give an LDH layer of thickness 65nm, a ratio of 2:1 was found to give an LDH layer of thickness 110nm and a layer of thickness of 160nm was obtained using a Mg:Al ratio of 3:1. TEM images are shown in Figure 15. Core-shell SiO₂@LDHs were also prepared according to the procedure described in Example 1 above using different sized SiO₂ microspheres, 300 nm, 550 nm and 800 nm. TEM images are shown in Figure 16. TEM images of the SiO₂@LDHs produced with different morphology (a) solid (Example 1), (b) yolk shell (Example 1 at 40°C) and (c) hollow (Example 1 at pH11), as described above, are shown in Figure 17.

Example 2

In order to obtain a 1:1 Mg:Al LDH, the procedure described above in Example 1 was repeated with the exception that an aqueous solution (19.2

mL) containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.72 mmol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.72 mmol) was added at a rate of 60 mL/h to solution A under vigorous stirring.

Example 3

In order to obtain a 3:1 Mg:Al LDH, the procedure described above in Example 1 was repeated with the exception that an aqueous solution (19.2 mL) containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.08 mmol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.36 mmol) was added at a rate of 60 mL/h to solution A under vigorous stirring.

The XRD patterns of the SiO_2 @LDH samples prepared with Mg:Al ratios of 1:1 (Example 2) and 3:1 (Example 3) are shown in Figure 12.

Example 4

The silica@LDH particles were synthesised via the coprecipitation method. Silica spheres (100 mg, 550 nm) were dispersed in deionised water (20 mL) using ultrasound treatment. After 30 min, the anion salt (0.96 mmol), Na_2CO_3 , was added to the solution containing ammonia (0.8 mL, 35%) and a further 5 min of sonication was carried out to form solution A. Next an aqueous solution (19.2 mL) containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.96 mmol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.48 mmol) was added at a rate of 60 mL/h to solution A under vigorous stirring. The obtained solid was collected with centrifugation at 4000 rpm for 5 min and then re-dispersed in deionised water (40 mL) and stirred for 1 h. The collection and re-dispersion were repeated twice. Afterward, the solid was washed with acetone (40 mL) and then re-dispersed in acetone (40 mL) and left to stir overnight. The solid was then dried under vacuum. The suspension was then dried under vacuum for materials characterisation.

The features disclosed in the foregoing description, in the claims as well as in the accompanying drawings, may both separately and in any combination thereof be material for realizing the invention in diverse forms thereof.

Example 5

In order to obtain Silica@AMO-LDHs in Mg : Al = 3 : 1. Synthesise the Silica@LDH particles by using the co-precipitation method, disperse silica spheres (100 mg) in the deionised water (20 mL) by using ultrasound treatment for 30 min, add the anion salt Na₂CO₃ (0.96 mmol) in the solution and further treat by ultrasound for 5 min, the finally solution named A. Then add an aqueous solution (19.2 mL) containing (1.08 mmol) Mg²⁺ and (0.36 mmol) Al³⁺ in the solution A at the rate of 60 mL/h with vigorous stirring. The pH of the reaction solution is controlled with the addition of 1 M NaOH by an autotitrator. And the morphology of Silica@LDH is controlled by pH and temperature. The obtained solid is collected with centrifugation at 5000 rpm for 5 min and then re-dispersed in deionised water (40mL) and stir for 1 h, the washing need repeated twice. Before final isolation, the solid is washed with acetone (40mL) and left to stir over night, and the suspension is then dried under vacuum

Example 6

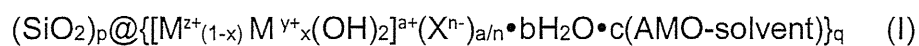
In order to obtain Silica@AMO-LDHs in Mg : Ni : Al = 2.7 : 0.3 : 1. The Silica@LDH particles will be synthesized by using the co-precipitation method, disperse silica spheres (100 mg) in the deionised water (20 mL) by using ultrasound treatment for 30 min, add the anion salt Na₂CO₃ (0.96 mmol) in the solution and further treat by ultrasound for 5 min, the finally solution named A. Then add an aqueous solution (19.2 mL) containing (0.972 mmol) Mg²⁺, (0.108 mmol) Ni²⁺ and (0.36 mmol) Al³⁺ in the solution A at the rate of 60 mL/h with vigorous stirring. The pH of the reaction solution is controlled with the addition of 1 M NaOH by an autotitrator. As followed the morphology of Silica@LDH is controlled by pH and temperature. The obtained solid is collected with centrifugation at 5000 rpm for 5 min and then re-dispersed in deionised water (40mL) and stir for 1 h, the washing need repeated twice. Before final isolation, the solid is washed with acetone (40mL) and left to stir over night, and the suspension is then dried under vacuum.

Example 7

In order to obtain Silica@AMO-LDHs in $\text{Mg} : \text{Al} : \text{Fe} = 3 : 0.9 : 0.1$. The Silica@LDH particles synthesise using the co-precipitation method, disperse silica spheres (100 mg) in the deionised water (20 mL) by using ultrasound treatment for 30 min, add the anion salt Na_2CO_3 (0.96 mmol) in the solution and further treat by ultrasound for 5 min, the finally solution named A. Then add an aqueous solution (19.2 mL) containing (1.08 mmol) Mg^{2+} , (0.324 mmol) Al^{3+} and (0.036 mmol) Fe^{3+} in the solution A at the rate of 60 mL/h with vigorous stirring. The pH of the reaction solution is controlled with the addition of 1 M NaOH by an autotitrator. As followed the morphology of Silica@LDH is controlled by pH and temperature. The obtained solid is collected with centrifugation at 5000 rpm for 5 min and then re-dispersed in deionised water (40mL) and stir for 1 h, the washing need repeated twice. Before final isolation, the solid is washed with acetone (40mL) and left to stir over night, and the suspension is then dried under vacuum

CLAIMS

1. A method of making silica-layered double hydroxide microspheres having the formula I



wherein,

M^{z+} and M^{y+} are two different charged metal cations;

$z = 1$ or 2 ;

$y = 3$ or 4 ;

$0 < x < 0.9$;

b is 0 to 10 ;

c has a value that is greater than zero and up to 10 ;

$p > 0$,

$q > 0$,

X^{n-} is an anion; with $n > 0$

$a = z(1-x) + xy-2$; and

the AMO-solvent is an 100% aqueous miscible organic solvent;

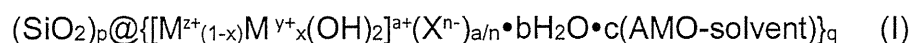
which method comprises the steps:

- (a) contacting silica microspheres and a metal ion containing solution containing metal ions M^{z+} and M^{y+} in the presence of a base and an anion solution;
- (b) collecting the product; and

- (c) treating the product with AMO-solvent and recovering the solvent treated material to obtain the silica-layered double hydroxide microspheres of formula (I).
2. The method according to claim 1, wherein M' is one or more trivalent metal cations.
 3. The method according to claim 1 or 2, wherein M is one or more divalent metal cations.
 4. The method according to any of the preceding claims, wherein X^{n-} is selected from CO_3^{2-} , OH^- , F^- , Cl^- , Br^- , I^- , SO_4^{2-} , NO_3^- and PO_4^{3-} , preferably from CO_3^{2-} , Cl^- and NO_3^- , or a mixture of two or more thereof.
 5. The method according to any of the preceding claims, wherein M is Mg, M is Al and X^{n-} is CO_3^{2-} .
 6. The method according to any of the preceding claims, wherein the pH of the metal ion containing solution in step (a) is within a range from 8 to 12.
 7. The method according to claim 6, wherein the pH is of from 9 to 10.
 8. The method according to any one of the preceding claims, wherein the product collected in step (b) is dispersed in the AMO-solvent and wherein c in the formula I has a value which is greater than zero and up to 10.

9. The method according to claim 8, wherein the dispersion of the product in the AMO-solvent is maintained for 2 or more hours and then the treated material is separated from the solvent.
10. The method according to any of the preceding claims, wherein the AMO-solvent is acetone, ethanol or methanol or a mixture thereof, preferably acetone or ethanol.
11. The method according to any of the preceding claims, wherein the temperature of the metal ion containing solution in step (a) is within a range of from 20 to 150°C.
12. The method according to claim 11, wherein the temperature is from 20 to 80°C.
13. The method as claimed in any one of the preceding claims, wherein the silica-layered double hydroxide microspheres have specific surface area as determined by N₂ BET of at least 177 m²/g, preferably at least 200 m²/g.
14. The method as claimed in any of the preceding claims, wherein the silica-layered double hydroxide microspheres have at least one structure from hollow-shell, yolk-shell and solid core-shell structures.
15. The method as claimed in any of the preceding claims, wherein the silica-layered double hydroxide microspheres have a thickness of layered double hydroxide layer larger than 65 nm, preferably larger than 110 nm, more preferably larger than 160 nm.

16. Silica-layered double hydroxide microspheres having the formula I below



wherein,

M^{z+} and M^{y+} are two different charged metal cations;

$z = 1$ or 2 ;

$y = 3$ or 4 ;

$0 < x < 0.9$;

b is 0 to 10 ;

c is 0 to 10 ;

$p > 0$,

$q > 0$;

X^{n-} is an anion; with $n > 0$;

$a = z(1-x) + xy-2$; and

AMO-solvent is an 100% aqueous miscible organic solvent,

wherein the silica-layered double hydroxide microspheres each comprise a SiO_2 microsphere having solid layered double hydroxide attached to its surface, and wherein:

- i. the silica-layered double hydroxide microspheres are core-shell materials wherein the SiO_2 microsphere is a solid sphere, and wherein the specific surface area of the core-shell materials is at least $100 \text{ m}^2/\text{g}$, or
- ii. the silica-layered double hydroxide microspheres are yolk-shell materials wherein the SiO_2 microsphere comprises an outer shell and a smaller SiO_2 sphere contained within the outer shell, wherein there is a hollow portion between the smaller sphere and the inner surface of the

- outer shell, and wherein the specific surface area of the yolk-shell materials is at least 100 m²/g, or
- iii. the silica-layered double hydroxide microspheres are hollow shell materials wherein the SiO₂ microsphere has a hollow interior, and wherein the hollow shell materials have a specific surface area of at least 130 m²/g.
17. Silica-layered double hydroxide microspheres according to claim 16, wherein M' is one or more trivalent cations.
 18. Silica-layered double hydroxide microspheres according to claim 16 or 17, wherein M is one or more divalent cations.
 19. Silica-layered double hydroxide microspheres according to any one of claims 16 to 18, wherein Xⁿ⁻ is selected from CO₃²⁻, OH⁻, F⁻, Cl⁻, Br⁻, I⁻, SO₄²⁻, NO₃⁻ and PO₄³⁻, preferably from CO₃²⁻, Cl⁻ and NO₃⁻, or mixtures thereof.
 20. Silica-layered double hydroxide microspheres according to any one of the claims 16 to 19, wherein M is Mg, M' is Al and Xⁿ⁻ is CO₃²⁻.
 21. Silica-layered double hydroxide microspheres according to any one of claims 16 to 20, wherein the AMO- solvent is acetone, ethanol, methanol or mixtures thereof, preferably acetone or ethanol.
 22. Silica-layered double hydroxide microspheres according to claim 16, wherein M²⁺ is a divalent metal cation,

M^{y+} is a trivalent metal cation, and
each of b and c is a number $>$ zero.