

## METHOD OF SYNTHESIZING A LAYERED DOUBLE HYDROXIDE

### CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of US provisional application No. 61/907,656 filed on 22 November 2013, the content of which is incorporated herein by reference in its entirety for all purposes.

### TECHNICAL FIELD

[0002] The invention relates to layered double hydroxide.

### BACKGROUND

[0003] Supercapacitors, a promising energy storage device, have received tremendous amount of attention because of their high power density and excellent cycle life. In particular, pseudocapacitive electrode materials, which possess reversible faradic reaction behavior, are of great interests for high energy density storage applications, with performance comparable to that of carbon based materials.

[0004] Layered double hydroxides (LDHs) have generated considerable attention in supercapacitor applications due to their unique structure. Generally, structure of LDHs includes metal-hydroxyl host slab layers and charge-balancing anions between the layers. This enables a large variety of functionality and hybrid possibility for potential applications, such as anion exchangers, UV absorbents, catalysts, and drug delivery systems. LDHs are of particular interest in electrochemical applications, where large interlayer spacings of the LDHs provide enhanced accessibility of electrolyte into reaction sites. Meanwhile, hydroxides of electrochemically redox active transition metal, such as those of cobalt (Co) and nickel (Ni), are favorable for high energy density storage as they usually possess high specific capacitances.

[0005] One of the main issues limiting electrochemical performance of LDHs relates to their poor rate performance. To fabricate supercapacitors with high energy storage/delivery at high power density, electrode material with improved electrochemical reaction rates and electron transfer rates are required. In most cases, current densities of LDHs do not exceed  $10 \text{ A g}^{-1}$ , while their specific capacitance drops dramatically at higher current densities, such as  $20 \text{ A g}^{-1}$ .

[0006] In view of the above, there exists a need for improved layered double hydroxides that overcome or at least alleviate one or more of the above-mentioned problems.

### SUMMARY

5 [0007] In a first aspect, a method of synthesizing a layered double hydroxide is provided. The method comprises forming the layered double hydroxide in presence of a steric repulsion agent, wherein amount of the steric repulsion agent is varied to control size of the layered double hydroxide formed.

[0008] In a second aspect, a layered double hydroxide formed by a method according to  
10 the first aspect is provided.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying  
15 drawings, in which:

[0010] **FIG. 1** is a schematic illustration of formation of micro-sized LDHs and nano-sized LDHs. **(A)** shows initial formation of LDH nuclei; **(B)** shows formation of micro-sized LDHs; **(C)** shows formation process in presence of a steric repulsion agent; and **(D)** shows formation of nano-sized LDHs.

20 [0011] **FIG. 2A** to **2E** are scanning electron microscopy (SEM) images of **(A)** nanosized Ni-Co LDH at low magnification prepared using gelatin; **(B)** nanosized Ni-Co LDH at high magnification prepared using gelatin; **(C)** nano-sized Ni-Co LDH at low magnification prepared using agarose; **(D)** micro-sized Ni-Co LDH at low magnification prepared using agarose; and **(E)** micro-sized Ni-Co LDH. Scale bar in **FIG. 2A, 2C** and **2E** denote 1  $\mu\text{m}$ ,  
25 and scale bar in **FIG. 2B** and **2D** denote 100 nm.

[0012] **FIG. 3A** is a graph showing cyclic voltammetry (CV) curves of micro-sized LDHs and nano-sized LDHs. **FIG. 3B** is a graph showing relationship between specific capacitance at different current densities and specific capacitances of micro- and nano-sized LDHs. **FIG. 3C** is a graph showing Nyquist plot of micro- and nano-sized LDHs.

30 [0013] **FIG. 4 (a)** and **(b)** are SEM images of Zn-Co LDHs; **(c)** and **(d)** are SEM images of Cu-Co LDHs; **(e)** and **(f)** are SEM images of Ni-Mn LDHs; Scale bar in **FIG. 4(a), (c)** and **(e)** denotes 1  $\mu\text{m}$ ; scale bar in **FIG. 4(b), (d)** and **(f)** denotes 100 nm.

[0014] FIG. 5(a) is a SEM image of Zn-Co LDHs and the boxed area is the energy dispersive X-ray element analysis (EDX) scan zone; (b) is an EDX spectrum of Zn-Co LDHs; (c) is a SEM image of Cu-Co LDHs and the boxed area is the EDX scan zone; (d) is an EDX spectrum of Cu-Co LDHs; (e) is a SEM image of Ni-Mn LDHs and the boxed area is the energy dispersive X-ray element analysis (EDX) scan zone; and (f) is an EDX spectrum of Ni-Mn LDHs. Scale bar in FIG. 5(a) and (c) denotes 6  $\mu\text{m}$ . Scale bar in FIG. 5(e) denotes 10  $\mu\text{m}$ .

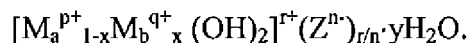
### DETAILED DESCRIPTION

[0015] In a first aspect, the invention refers to a method of synthesizing a layered double hydroxide (LDH). The method includes forming the layered double hydroxide in presence of a steric repulsion agent, wherein amount of the steric repulsion agent is varied to control size of the layered double hydroxide formed.

[0016] By forming a layered double hydroxide in presence of a steric repulsion agent, such as one or more biomacromolecules, crystal growth of layers or plates in the LDH may be restricted. In so doing, size of the LDHs formed may be reduced from the order of micrometers to nanometers. Nanosized LDHs may be formed as a result. By controlling or varying amount of the steric repulsion agent present, size of the LDHs formed may be controlled. Due to reduction in size of the LDH layers, electron conduction length as well as electrolyte diffusion length may be greatly reduced. This in turn translates into improvements in the rate capability of the LDH material, rendering the LDH material particularly suited for use in high performance supercapacitors. For example, it has been demonstrated herein that the nanosized LDHs possess a high specific capacitance of 1290 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup> and 720 F g<sup>-1</sup> at 30 A g<sup>-1</sup>. The nanosized LDHs disclosed herein are also beneficial for use in other electrochemical applications, such as electrochemical catalyst for oxygen evolution/reduction or aqueous based metal-air battery (like Zn-Air).

[0017] As used herein, the term "layered double hydroxide" (LDH), also known as "anionic clay" or "hydrotalcite-like compound", refers to a layered structure material having positively charged layers and charge balancing anions located between the layers in the interlayer regions. Apart from the charge balancing anions, water molecules may also be present in the interlayer regions.

[0018] The layered double hydroxide disclosed herein may be represented by general formula



5 [0019] In the formula,  $M_a^{p+}$  and  $M_b^{q+}$  are independently metal cations. In various embodiments,  $M_a^{p+}$  may be monovalent metal ions, or divalent metal ions.  $M_b^{q+}$  may be trivalent metal ions. Accordingly, p may be 1 or 2, and q may be 3.

[0020] The  $M_a^{p+}$  and  $M_b^{q+}$  metal cations may have similar ionic radii, and may be coordinated by six oxygen atoms forming  $M_a^{p+}/M_b^{q+}(OH)_6$  octahedra. These octahedra may form two-dimensional sheets via edge sharing and may stack together by hydrogen bonding between the hydroxyl groups of adjacent sheets. The  $M_a^{p+}$  and  $M_b^{q+}$  metal cations may occupy octahedral positions in the hydroxide layers.

[0021] Examples of metals which may be used to form  $M_a^{+}$  and/or  $M_b^{+}$  monovalent metal cations include lithium (Li). Examples of metals which may be used to form  $M_a^{2+}$  and/or  $M_b^{2+}$  divalent metal cations include cadmium (Cd), magnesium (Mg), manganese (Mn), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), and/or calcium (Ca). Examples of metals which may be used to form  $M_a^{3+}$  and/or  $M_b^{3+}$  trivalent metal cations include iron (Fe), chromium (Cr), gallium (Ga), aluminum (Al), manganese (Mn), and/or cobalt (Co).

[0022]  $M_a$  and  $M_b$  may be the same or different. In various embodiments,  $M_a$  and  $M_b$  are the same. For example,  $M_a$  and  $M_b$  may be cobalt, which may form  $Co^{2+}$  and/or  $Co^{3+}$  ions in the layered double hydroxide. In various embodiments,  $M_a$  and  $M_b$  are different. For example,  $M_a$  may be nickel and  $M_b$  may be cobalt, which may respectively form  $Ni^{2+}$ , and/or  $Co^{2+}$  and/or  $Co^{3+}$  ions in the layered double hydroxide.

[0023] In some embodiments, p is 1, and q is 3. Accordingly,  $M_a^{+}$  may be  $Li^{+}$ , and  $M_b^{3+}$  may be  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $Ga^{3+}$ ,  $Al^{3+}$ ,  $Mn^{3+}$ , and/or  $Co^{3+}$ .

[0024] In some embodiments, p is 2, and q is 3. Accordingly,  $M_a^{2+}$  may be  $Cd^{2+}$ ,  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ , and/or  $Ca^{2+}$ , while  $M_b^{3+}$  may be  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $Ga^{3+}$ ,  $Al^{3+}$ ,  $Mn^{3+}$ , and/or  $Co^{3+}$ .

[0025]  $Z^{n-}$  refers to a hydrated anion that is adapted to intercalate in the interlayer regions of the layered double hydroxide, and n denotes valency of the anion. Examples of  $Z^{n-}$  include a halide such as fluoride, chloride, bromide, and iodide, nitrate, carbonate, sulfate, phosphate, acetate, hydroxide, ferricyanide,  $C_6H_4-1,4-(CO_2)_2$ , dodecyl-sulfate,  $SiO(OH)_3$ , perchlorate ion,

oxalate, hydrogen phosphate, or  $n\text{-C}_a\text{H}_{2a+1}\text{SO}_4$ . Depending on the anion,  $n$  may be 1, 2 or 3. Accordingly,  $Z^{n-}$  may be selected from the group consisting of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{C}_2\text{H}_3\text{O}_2^-$ ,  $\text{OH}^-$ ,  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\text{C}_6\text{H}_4\text{-1,4-(CO}_2)_2^{2-}$ ,  $\text{C}_{12}\text{H}_{25}\text{SO}_4^-$ ,  $\text{SiO}(\text{OH})_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{HPO}_4^{2-}$ , or  $n\text{-C}_a\text{H}_{2a+1}\text{SO}_4^{2-}$ .

5 [0026] In various embodiments,  $Z^{n-}$  is selected from the group consisting of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , and  $\text{C}_2\text{H}_3\text{O}_2^-$ . In specific embodiments,  $Z^{n-}$  is  $\text{NO}_3^-$ .

[0027] Examples of layered double hydroxides that may be prepared using methods disclosed herein are provided, for example, in *Aamir I. Khan, J. Mater. Chem., 2002, 12, 3191-3198*.

10 [0028] The charge balancing anions may be weakly bound to the positively charged layers and may be exchangeable with one or more anionic species. As the layered double hydroxide may demonstrate selective intercalation properties and anions located in the interlayer regions may generally be easily replaced, the layered double hydroxide disclosed herein may be used as selective anion exchange materials with one or more anionic guest species. Intercalation of  
15 the anionic guest species may be achieved, for example, by direct synthesis, or ion-exchange of the charge balancing anions with the anionic guest species.

[0029]  $x$  may be a number in the range of 0 to 1, such as 0.1, 0.2, 0.3, 0.4, or 0.5. In various embodiments,  $x$  is a number between 0 and 1, exclusive. In some embodiments,  $x$  is a number in the range of 0.1 to 0.5.

20 [0030]  $y$  is a number representing moles of water, and may generally be in the range of 0.33 to 1.25. For example,  $y$  may in the range of 0.38 to 1.25, 0.5 to 1.25, 0.66 to 1.25, 0.7 to 1.25, 0.86 to 1.25, 0.38 to 1.05, 0.46 to 1.05, or 0.5 to 0.7.

[0031]  $r$  may be  $x$  when  $p$  is 2. When  $p$  is 1,  $r$  may be  $2x - 1$ .

[0032] The layered double hydroxide is formed in presence of a steric repulsion agent. As  
25 mentioned above, presence of a steric repulsion agent during preparation of a layered double hydroxide hinders or restricts formation of the layered double hydroxide. In so doing, size of the LDH layers may be reduced, and nanosized LDHs may be formed. By controlling or varying amount of the steric repulsion agent present, size of the LDHs formed may be controlled.

30 [0033] The steric repulsion agent may, for example, be one or more biomacromolecules. As used herein, the term "biomacromolecule" refers to a polymeric material that may be found in nature. Molecular weight of the biomacromolecule may be at least 20 kDa, such as

at least 25 kDa, at least 50 kDa, at least 75 kDa, at least 100 kDa, at least 125 kDa, or at least 150 kDa. The molecular weight may be expressed in terms of a number average molecular weight of the biomacromolecules present. In various embodiments, molecular weight of each biomacromolecule in the steric repulsion agent is at least 20 kDa, or at least 25 kDa.

5 [0034] Examples of a biomacromolecule include, but are not limited to, a protein, a polysaccharide, glycosaminoglycans, or a nucleic acid. Advantageously, biomacromolecules such as gelatin and agarose may function as green renewable structural directing reagents to form the nanosized LDHs. Biomacromolecules also allow large scale synthesis with high precursor concentration.

10 [0035] In various embodiments, the steric repulsion agent comprises or consists of one or more biomacromolecules. In some embodiments, the steric repulsion agent is a hydrogel comprising biomacromolecules. As used herein, the term "hydrogel" refers to a broad class of polymeric materials which have an affinity for an aqueous medium, and are able to absorb large amounts of the aqueous medium, but which do not normally dissolve in the aqueous  
15 medium. The biomacromolecules may act as hydrogel precursors, to set or solidify in an aqueous medium to form a three-dimensional network, wherein formation of the three-dimensional network may cause the biomacromolecules to gel into a hydrogel. The biomacromolecules may be present in a suitable concentration to allow formation of the hydrogel.

20 [0036] In various embodiments, the one or more biomacromolecules may be selected from the group consisting of protein, polysaccharide, nucleic acid, and combinations thereof. Suitable nucleic acids may be one that has a molecular weight in the range as mentioned above, and which is soluble in aqueous solution.

[0037] In some embodiments, the one or more biomacromolecules may be selected from  
25 the group consisting of protein, polysaccharide, and combinations thereof.

[0038] The one or more biomacromolecules may comprise or consist of a protein. Peptides, which form building blocks of polypeptides and in turn proteins, generally refer to short chains of amino acids linked by peptide bonds. Typically, peptides comprise amino acid chains of about 2-100, more typically about 4-50, and most commonly about 6-20 amino  
30 acids. Polypeptides generally refer to individual straight or branched chain sequences of amino acids that are typically longer than peptides. They usually comprise at least about 20 to 1000 amino acids in length, more typically at least about 100 to 600 amino acids, and

frequently at least about 200 to about 500 amino acids. Included are homo-polymers of one specific amino acid, such as for example, poly-lysine. Proteins include single polypeptides as well as complexes of multiple polypeptide chains, which may be the same or different.

[0039] Proteins have diverse biological functions and may be classified into five major categories, i.e. structural proteins such as collagen, catalytic proteins such as enzymes, transport proteins such as hemoglobin, regulatory proteins such as hormones, and protective proteins such as antibodies and thrombin.

[0040] In various embodiments, the protein is selected from the group consisting of gelatin, collagen, albumin, casein, lactoglobulin, and combinations thereof. In specific embodiments, the one or more biomacromolecules comprises or consists of gelatin.

[0041] The term "gelatin" as used herein refers to protein substances derived from collagen. In the context of the present invention, the term "gelatin" also refers to equivalent substances such as synthetic analogues of gelatin. Generally, gelatin may be classified as alkaline gelatin, acidic gelatin, or enzymatic gelatin. Alkaline gelatin may be obtained from the treatment of collagen with a base such as sodium hydroxide or calcium hydroxide. Acidic gelatin may be obtained from the treatment of collagen with an acid such as hydrochloric acid. Enzymatic gelatin may be obtained from the treatment of collagen with an enzyme such as hydrolase.

[0042] In some embodiments, the one or more biomacromolecules comprises or consists of a polysaccharide. Polysaccharides are carbohydrates which can be hydrolyzed to two or more monosaccharide molecules. They can contain a backbone of repeating carbohydrate i.e. sugar unit. For example, the polysaccharide may be selected from the group consisting of agarose, alginate, chitosan, dextran, soluble starch, gellan gum, and combinations thereof. Glycosaminoglycans are polysaccharides containing amino sugars as a component. Examples of glycosaminoglycans include, but are not limited to, hyaluronic acid, chondroitin sulfate, dermatin sulfate, keratin sulfate, dextran sulfate, heparin sulfate, heparin, glucuronic acid, iduronic acid, galactose, galactosamine, and glucosamine.

[0043] In specific embodiments, the one or more biomacromolecules comprises or consists of agarose. Agarose refers to a neutral gelling fraction of a polysaccharide complex extracted from the agarocytes of algae such as a Rhodophyceae. However, unlike alginate, it forms thermally reversible gels.

[0044] Besides the above-mentioned, a combination of protein and polysaccharide may also be used. For example, the steric repulsion agent may comprise gelatin and agarose.

[0045] Forming the layered double hydroxide in presence of a steric repulsion agent may include providing a first solution comprising the steric repulsion agent; dissolving at least one metal salt in the first solution comprising the steric repulsion agent to form a second solution; adding a precipitating agent to the second solution to form a third solution; and heating the third solution to obtain the layered double hydroxide.

[0046] In various embodiments, providing a first solution comprising the steric repulsion agent comprises at least substantially dissolving the steric repulsion agent in a liquid reagent.

The liquid reagent may be an aqueous solution, such as water or a solution based primarily on water such as water containing a salt dissolved therein. In specific embodiments, the steric repulsion agent is completely dissolved in the liquid reagent.

[0047] Concentration of the steric repulsion agent in the first solution may be in the range of about 0.1 wt% to about 1 wt%, such as about 0.1 wt% to about 0.8 wt%, about 0.1 wt% to about 0.6 wt%, about 0.1 wt% to about 0.4 wt%, about 0.3 wt% to about 1 wt%, about 0.5 wt% to about 1 wt%, about 0.3 wt% to about 0.8 wt%, about 0.2 wt% to about 0.6 wt%, or about 0.1 wt%, about 0.3 wt% or about 0.5 wt%.

[0048] At least one metal salt may be dissolved in the first solution comprising the steric repulsion agent to form a second solution. The at least one metal salt may be at least substantially soluble in the first solution. In specific embodiments, the at least one metal salt is completely soluble in the first solution. In embodiments where the method includes dissolving the steric repulsion agent in the first solution comprising the steric repulsion agent to form a second solution, the at least one metal salt may be dissolved at the same time as or after the steric repulsion agent has been dissolved in the liquid reagent.

[0049] In various embodiments, the at least one metal salt is dissolved after the steric repulsion agent has been dissolved in the liquid reagent. By having the steric repulsion agent present in the first solution, prior to dissolving the at least one metal salt in the first solution, size of the layered double hydroxide formed may be more effectively controlled.

[0050] The at least one metal salt may be a metal salt containing anions such as those described above. In various embodiments, the at least one metal salt is selected from the group consisting of a metal nitrate, a metal halide, a metal sulfate, and a metal acetate. In some embodiments, the at least one metal salt is a metal nitrate.

[0051] Suitable metals that may be comprised in the metal salts to form the layered double hydroxides have already been described above. In some embodiments, the at least one metal salt may be a salt of a metal selected from the group consisting of lithium, cadmium, magnesium, cobalt, nickel, copper, zinc, manganese, iron, chromium, gallium, aluminum, calcium, and combinations thereof. In specific embodiments, the at least one metal salt may be a salt of a metal selected from the group consisting of magnesium, cobalt, nickel, copper, zinc, manganese, iron, calcium, and combinations thereof.

[0052] Depending on the specific layered double hydroxides to be prepared, a combination of two metal salts may be used. In various embodiments, the at least one metal salt is a combination of two metal salts selected from the group consisting of a magnesium salt and a cobalt salt, a nickel salt and a cobalt salt, a copper salt and a cobalt salt, a zinc salt and a cobalt salt, a nickel salt and a manganese salt, and a nickel salt and an iron salt.

[0053] In some embodiments, the at least one metal salt comprises or consists of nickel nitrate and cobalt nitrate. This may be used to form Ni-Co layered double hydroxide, for example. Concentration of the nickel nitrate and cobalt nitrate may be about 1:1. As another example, to form Zn-Co layered double hydroxide, a combination of zinc nitrate and cobalt nitrate may be used. As a further example, a combination of cobalt nitrate and copper nitrate may be used to form Cu-Co layered double hydroxide.

[0054] Concentration of metal ions in the second solution may be in the range of about 30 mM to about 60 mM. For example, concentration of metal ions in the second solution may be in the range of about 30 mM to about 40 mM, about 30 mM to about 50 mM, about 40 mM to about 60 mM, about 50 mM to about 60 mM, about 40 mM to about 50 mM, about 30 mM, or about 40 mM.

[0055] Forming the layered double hydroxide in presence of a steric repulsion agent may include adding a precipitating agent to the second solution to form a third solution. The precipitating agent may be added at the same time as the at least one metal salt into the first solution, or may be added after the at least one metal salt has been dissolved in the first solution. For example, the precipitating agent may be added to the second solution comprising the at least one metal salt.

[0056] In various embodiments, the precipitating agent is selected from the group consisting of hexamethylenetetramine, urea, thiourea, and combinations thereof. Concentration of the precipitating agent in the third solution may be in the range of about 0.1

M to about 0.5 M, such as about 0.1 M to about 0.4 M, about 0.1 M to about 0.3 M, about 0.2 M to about 0.5 M, about 0.3 M to about 0.5 M, about 0.2 M to about 0.4 M, or about 0.3 M to about 0.4 M.

[0057] The third solution may be heated to obtain the layered double hydroxide. The heating may be carried out in an open vessel such as a flask, or in a closed vessel such as in an autoclave. In various embodiments, heating the third solution is carried out at a temperature in the range of about 80 °C to about 120 °C. In case the heating is carried out in a closed vessel, a higher temperature may be used. For example, heating the third solution may be carried out at a temperature of about 80 °C to about 100 °C in a flask, while in a closed vessel such as an autoclave, heating the third solution may be carried out at a temperature of about 80 °C to about 120 °C, such as about 100 °C to about 120 °C.

[0058] Heating the third solution may be carried out for any suitable time period that is able to form the layered double hydroxide. For example, heating the third solution may be carried out for a time period in the range of about 5 hours to about 14 hours, such as about 5 hours to about 10 hours, about 5 hours to about 8 hours, about 8 hours to about 14 hours, about 10 hours to about 14 hours, about 6 hours to about 12 hours, or about 8 hours to about 12 hours.

[0059] As mentioned above, a combination of two metal salts may be used depending on the specific layered double hydroxides to be prepared. Besides dissolving a combination of two metal salts comprising a first metal salt and a second metal salt in a first solution to form a second solution, the first metal salt and the second metal salt may be added separately, and which may be carried out in two separate steps. For example, a first metal salt may first be dissolved in a first solution to form a second solution. Subsequently, after addition of a precipitating agent in the second solution to form a third solution, and while heating the third solution, a second metal salt may be added into the third solution. Advantageously, by separately adding the first metal salt and the second metal salt, any possible phase separation caused by different  $K_{sp}$  of metal hydroxides may be eliminated.

[0060] Accordingly, in various embodiments, heating the third solution comprises adding a second metal salt into the third solution. The second metal salt may comprise a metal different from the metal in the first metal salt. In specific embodiments, the first metal salt is cobalt nitrate, and the second metal salt is zinc nitrate or copper nitrate. Zn-Co LDH or Cu-Co LDH may accordingly be formed.

[0061] Concentration of the second metal salt in the third solution may be in the range of about 5 mM to about 15 mM, such as about 5 mM to about 10 mM, about 10 mM to about 15 mM, or about 8 mM to about 12 mM.

[0062] The method of the first aspect may include separating the layered double hydroxide that is formed. This may be carried out, for example, by filtering or centrifuging the third solution after heating.

[0063] Following the separation such as centrifugation, the layered double hydroxide may be dried. Drying the layered double hydroxide may be carried out at a temperature in the range of about 50 °C to about 70 °C, such as about 50 °C to about 60 °C, about 60 °C to about 70 °C, or about 55 °C to about 65 °C.

[0064] Drying the layered double hydroxide may be carried out for any suitable time period for drying the layered double hydroxide. Generally, drying the layered double hydroxide may be carried out for a few hours. In various embodiments, drying the layered double hydroxide is carried out for a time period of at least 6 hours.

[0065] As mentioned above, by using a steric repulsion agent, such as one or more biomacromolecules, during preparation of the layered double hydroxide, crystal growth of layered double hydroxide layers or plates may be restricted, and nanosized layered double hydroxides may be formed. In various embodiments, the layered double hydroxide is a nanosized layered double hydroxide.

[0066] As the layered double hydroxide may not be regular in shape, size of the layered double hydroxide may be characterized by its maximal dimension, which refers to maximal length of the layered double hydroxide in any direction. The maximal dimension of the layered double hydroxide may be expressed in terms of an average value of the maximal dimension of the layered double hydroxides. For example, maximal dimension of the layered double hydroxides may be less than 300 nm, such as less than 250 nm, less than 200 nm, less than 150 nm, or less than 100 nm.

[0067] In various embodiments, each layered double hydroxide may have a maximal dimension of less than 300 nm, such as less than 250 nm, less than 200 nm, less than 150 nm, or less than 100 nm. In some embodiments, maximal dimension of each layered double hydroxide is in the range of between about 100 nm to about 300 nm, such as about 200 nm to about 300 nm, about 150 nm to about 250 nm, or about 100 nm to about 200 nm.

[0068] The invention also refers in a further aspect to a layered double hydroxide prepared by a method according to the first aspect.

[0069] Advantageously, it has been demonstrated herein that significant improvements in terms of electrochemical properties for high performance supercapacitors as a result of reduction of size of layered double hydroxides used to below 300 nm, such as below 200 nm, where electron conduction length and electrolyte diffusion length are greatly reduced. Other advantages include use of green renewable structural directing reagent such as gelatin and agarose in the manufacturing process, which is environmentally friendly. Further, the method may be adopted easily in industrial scale production.

[0070] Hereinafter, the present invention will be described more fully with reference to the accompanying drawings, in which exemplary embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the exemplary embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. In the drawings, lengths and sizes of layers and regions may be exaggerated for clarity.

[0071] As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items. The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used herein, the singular forms "a", "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises" and/or "comprising," when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof.

[0072] Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

[0073] The invention illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed  
5 herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional  
10 features, modification and variation of the invention embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[0074] The invention has been described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form  
15 part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[0075] Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups,  
20 those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

## EXPERIMENTAL SECTION

[0076] In various embodiments, a facile preparation method of nanosized Ni Co LDHs  
25 material is introduced. Renewable bio macromolecule (gelatin/agarose) is used as a steric repulsion reagent to restrict crystal growth of large LDHs plates. Generally, LDHs show a 2D plate morphology, where diameter of the material is above several micrometers. By applying gelatin, diameter of LDHs is greatly reduced to a range of about 100 nm to about 200 nm. As a result, electron conduction length as well as electrolyte diffusion length is greatly reduced.  
30 The nanosized LDHs show a high specific capacitance of 1290 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup> and 720 F g<sup>-1</sup> at 30 A g<sup>-1</sup>, indicating an outstanding rate capability.

[0077] Advantages of nanosized LDHs material disclosed herein include (i) use of green renewable structural directing reagent gelatin and agarose; and (ii) significant improvements in terms of electrochemical properties for high performance supercapacitors due to (a) reduction of material size to one that is below about 300 nm, such as below about 200 nm; and (b) great reduction in electron conduction length and electrolyte diffusion length.

[0078] Various embodiments relate to the method synthesis of nano-sized Ni Co LDHs material in an effort to enhance the electron conduction as well as the electrolyte diffusion for the benefit of high energy density supercapacitors.

[0079] **Example 1: Synthesis of micro-sized and nano-sized LDHs material**

[0080] Gelatin/Agarose was dissolved in hot DI water at a ratio of 0.1 wt % to form a solution.  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Co}(\text{NO}_3)_2$  were dissolved in the solution to obtain 40 mM metal ion concentration (Ni:Co = 1:1). Hexamethylenetetramine (HMTA) was subsequently dissolved in the solution to get a 0.2 M concentration.

[0081] The reaction was carried out at known fixed temperature (80 °C) in flask. After a further 5 hours of reaction, the green product was collected by centrifugation. After the reaction, the product was washed several times with ethanol and distilled water followed by drying at 60 °C for 6 hours. For the synthesis of micro-sized LDHs, there is no addition of gelatin in the first step.

[0082] The morphologies of nano-sized LDHs prepared by gelatin are shown in FIG. 2A and FIG. 2B. The morphologies of nano-sized LDHs prepared by agarose are shown in FIG. 2C and FIG. 2D. Morphologies of micro-sized LDHs prepared without bio macromolecular are shown in FIG. 2E.

[0083] **Example 2: Electrochemical characterizations of micro- and nano-sized LDHs materials**

[0084] FIG. 3A shows the CV curves of micro- and nano- sized LDHs. The nano-sized LDHs show a more well-defined CV curves with smaller cathodic-anodic peaks separation, which indicates more facile electron transfer kinetics of nano-sized LDHs. FIG. 3B shows the relationships between different current densities and specific capacitances. It may be seen that micro-sized LDHs experience a sharp decrease in specific capacitance at higher current densities.

[0085] On the contrary, nanosized LDHs have much better capacitance retention comparing with micro-sized LDHs. Even at a high current density of 30 A g<sup>-1</sup>, the specific

capacitance of nano-sized LDHs could maintain  $720 \text{ F g}^{-1}$ . FIG. 3C shows the Nyquist plots of micro- and nano-sized LDHs. At low frequency region, the nano-sized LDHs show a more vertical response than micro-sized LDHs. It suggests that the electrolyte diffusion is more facile in nano-sized LDHs, meanwhile the nanosized LDHs have better capacitor behavior.

5 [0086] **Example 3: Comparison of the rate performance with previous publications**

[0087] TABLE 1 shows the summary of electrochemically active LDHs and their composite materials. For all the references, the diameters of LDHs are over several micro meters. The rate performance of nanosized LDHs is superior to all the pristine LDHs (Ref. T2, T4, T7, T8, T9), while also having high specific capacitance over  $1200 \text{ F g}^{-1}$ . In addition, rate performance of nano-sized LDHs is superior to those LDHs-composite materials (Ref. T1, T3, T10).

[0088] TABLE 1: Literature summary of layered double hydroxides.

| Material      | Synthesis method                  | Reference | Csp F/g | Remarks                                                   |
|---------------|-----------------------------------|-----------|---------|-----------------------------------------------------------|
| Co-Al LDHs    | LBL assembly with GO              | Ref. T1   | 1200    | complicated, low mass                                     |
|               | Electrochemical deposition        | Ref. T2   | 500     | low loading mass                                          |
|               | self assembly of GO and LDH       | Ref. T3   | 1031    | poor rate performance                                     |
|               | precipitation method              | Ref. T4   | 300~400 | $\text{K}_3\text{Fe}(\text{CN})_6$ redox mediator         |
|               | LHs-CNT composite                 | Ref. T5   | 342.4   | 192 for LHs only                                          |
|               | LHs-PEDOT                         | Ref. T6   | 672     | 63 % retention at $40 \text{ Ag}^{-1}$                    |
| Ni-Al LDHs    | ECD Ni foam                       | Ref. T7   | 701     |                                                           |
| Ni-Co LDHs    | hollow sphere                     | Ref. T8   | 2500    | poor rate performance                                     |
|               | particle, co-precipitation method | Ref. T9   | 2614    | poor rate performance                                     |
| Ni-Co-Al LDHs | Ni-Co-Al LHs and CNT composite    | Ref. T10  | 1100    | 57 % at $10 \text{ Ag}^{-1}$                              |
| Ni-Co LDHs    | Nano-sized Ni-Co LDHs             | This work | 1290    | 890 at $20 \text{ Ag}^{-1}$ , 720 at $30 \text{ Ag}^{-1}$ |

[0089] **References:**

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[Ref. T9] L. J. Xie, Z. A. Hu, C. X. Lv, G. H. Sun, J. L. Wang, Y. Q. Li, H. W. He, J. Wang, K. X. Li, Electrochimica Acta 2012, 78, 205.

15 [Ref. T10] J. Yang, C. Yu, X. M. Fan, Z. Ling, J. S. Qiu, Y. Gogotsi, Journal of Materials Chemistry A 2013, 1, 1963.

[0090] **Example 4: Synthesis of nano-sized Zn-Co LDHs (layered double hydroxides) and Cu-Co LDHs**

[0091] Gelatin/Agarose was dissolve in hot DI water with a ratio of 0.1 wt %  $\text{Co}(\text{NO}_3)_2$  was dissolved in the solution to get a 30 mM metal ion concentration.

20 Hexamethylenetetramine (HMTA) was dissolved in the resulting solution to obtain a 0.2 M concentration. The reaction was carried out at known fixed temperature (80 °C) in a flask without any stirring. After a further 0.5 hours of reaction,  $\text{Zn}(\text{NO}_3)_2$  or  $\text{Cu}(\text{NO}_3)_2$  was added into the flask to give a concentration of 10 mM. After another 4.5 hours, the green product was collected by centrifugation. After the reaction, the product was washed several times

25 with ethanol and distilled water followed by drying at 60 °C for 6 hours. The SEM images of corresponding products are shown in FIG. 4. The products all show nano-plate like structure with lateral dimension around 200 nm and thickness less than 20 nm.

[0092] **Example 5: Elemental information of Zn-Co LDHs and Cu-Co LDHs**

[0093] FIG. 5 shows the elemental information of Zn-Co LDHs and Cu-Co LDHs. The

30 presence of Zn, Co and Cu are confirmed in corresponding products. The mole ratio between Zn and Co is determined to be 0.73 : 1 and Cu: Co is 1.05 :1. The elemental ratio difference

between products and starting reagent ratio is due to the different solubility constant ( $K_{sp}$ ) of zinc hydroxide, cobalt hydroxide and copper hydroxides.

[0094] While the present invention has been particularly shown and described with reference to exemplary embodiments thereof, it will be understood by those of ordinary skill  
5 in the art that various changes in form and details may be made therein without departing from the spirit and scope of the present invention as defined by the following claims.

## CLAIMS

1. A method of synthesizing a layered double hydroxide, the method comprising forming the layered double hydroxide in presence of a steric repulsion agent, wherein  
5 amount of the steric repulsion agent is varied to control size of the layered double hydroxide formed.
2. The method according to claim 1, wherein forming the layered double hydroxide in presence of a steric repulsion agent comprises  
10
  - a) providing a first solution comprising the steric repulsion agent,
  - b) dissolving at least one metal salt in the first solution comprising the steric repulsion agent to form a second solution,
  - c) adding a precipitating agent to the second solution to form a third solution, and
  - d) heating the third solution to obtain the layered double hydroxide.
- 15 3. The method according to claim 1 or 2, wherein the steric repulsion agent comprises or consists of one or more biomacromolecules.
4. The method according to any one of claims 1 to 3, wherein the steric repulsion agent  
20 is a hydrogel comprising biomacromolecules.
5. The method according to claim 3 or 4, wherein the one or more biomacromolecules is selected from the group consisting of protein, polysaccharide, and combinations thereof.
- 25 6. The method according to claim 5, wherein the protein is selected from the group consisting of gelatin, collagen, albumin, casein, lactoglobulin, and combinations thereof.
- 30 7. The method according to claim 5 or 6, wherein the polysaccharide is selected from the group consisting of agarose, alginate, chitosan, dextran, soluble starch, gellan gum, and combinations thereof.

8. The method according to any one of claims 1 to 7, wherein the steric repulsion agent comprises gelatin, agarose, or combinations thereof.
- 5 9. The method according to any one of claims 2 to 8, wherein providing a first solution comprising the steric repulsion agent comprises at least substantially dissolving the steric repulsion agent in a liquid reagent
10. The method according to claim 9, wherein the liquid reagent is an aqueous solution.
- 10 11. The method according to any one of claims 2 to 10, wherein concentration of the steric repulsion agent in the first solution is in the range of about 0.1 wt% to about 1 wt%.
- 15 12. The method according to any one of claims 2 to 11, wherein the at least one metal salt is selected from the group consisting of a metal nitrate, a metal halide, a metal sulfate, and a metal acetate.
13. The method according to any one of claims 2 to 12, wherein the at least one metal salt is a salt of a metal selected from the group consisting of magnesium, cobalt, nickel, copper, zinc, manganese, iron, calcium, and combinations thereof.
- 20 14. The method according to any one of claims 2 to 13, wherein the at least one metal salt is a combination of two metal salts selected from the group consisting of a magnesium salt and a cobalt salt, a nickel salt and a cobalt salt, a copper salt and a cobalt salt, a zinc salt and a cobalt salt, a nickel salt and a manganese salt, and a nickel salt and an iron salt.
- 25 15. The method according to any one of claims 2 to 14, wherein concentration of metal ions in the second solution is in the range of about 30 mM to about 60 mM.
- 30

16. The method according to any one of claims 2 to 15, wherein the at least one metal salt in the second solution comprises or consists of nickel nitrate and cobalt nitrate.
- 5 17. The method according to claim 16, wherein ratio of nickel nitrate to cobalt nitrate is about 1:1.
18. The method according to any one of claims 2 to 17, wherein the precipitating agent is selected from the group consisting of hexamethylenetetramine, urea, thiourea, and combinations thereof.
- 10 19. The method according to any one of claims 2 to 18, wherein concentration of the precipitating agent in the third solution is in the range of about 0.1 M to about 0.5 M.
20. The method according to any one of claims 2 to 19, wherein heating the third solution is carried out at a temperature in the range of about 80 °C to about 120 °C.
- 15 21. The method according to any one of claims 2 to 20, wherein heating the third solution is carried out in an autoclave.
- 20 22. The method according to any one of claims 2 to 21, wherein heating the third solution is carried out for a time period in the range of about 5 hours to about 14 hours.
23. The method according to any one of claims 2 to 22, wherein heating the third solution comprises adding a second metal salt to the third solution.
- 25 24. The method according to claim 23, wherein the second metal salt comprises a metal different from the metal in the at least one metal salt in the second solution.
- 25 25. The method according to claim 23 or 24, wherein the at least one metal salt in the second solution is cobalt nitrate, and the second metal salt is zinc nitrate or copper nitrate.
- 30

26. The method according to any one of claims 23 to 25, wherein concentration of the second metal salt in the third solution is in the range of about 5 mM to about 15 mM.
27. The method according to any one of claims 2 to 26, further comprising centrifuging the third solution after heating.
28. The method according to claim 27, further comprising drying the layered double hydroxide at a temperature in the range of about 50 °C to about 70 °C.
29. The method according to claim 28, wherein drying the layered double hydroxide is carried out for a time period of at least 6 hours.
30. The method according to any one of claims 1 to 29, wherein the layered double hydroxide is a nanosized layered double hydroxide.
31. The method according to any one of claims 1 to 30, wherein the layered double hydroxide has a maximal dimension of about 300 nm.
32. The method according to any one of claims 1 to 31, wherein the layered double hydroxide has a maximal dimension of about 200 nm.
33. A layered double hydroxide prepared by a method according to any one of claims 1 to 32.